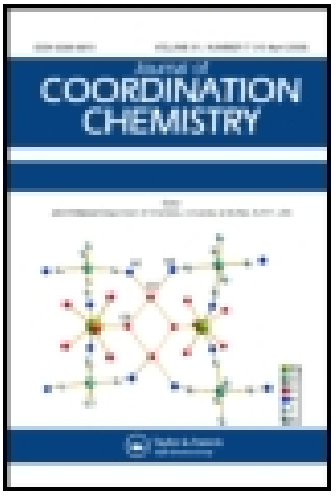

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New organotin(IV) complexes with N(4)-methylthiosemicarbazone derivatives prepared from 2,3-dihydroxybenzaldehyde and 2-hydroxy-5-methylbenzaldehyde: synthesis, characterization, and cytotoxic activity

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New organotin(IV) complexes with *N*(4)-methylthiosemicarbazone derivatives prepared from 2,3-dihydroxybenzaldehyde and 2-hydroxy-5-methylbenzaldehyde: synthesis, characterization, and cytotoxic activity

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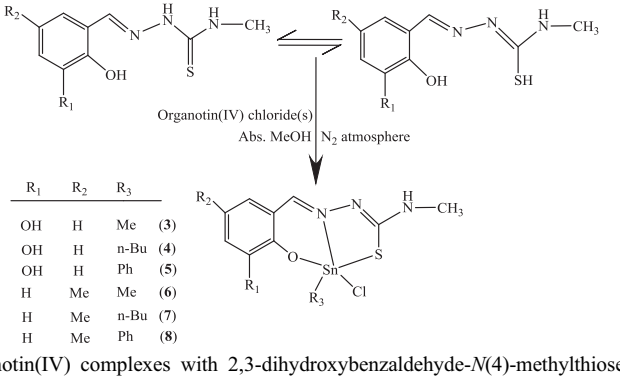

R_1	R_2	R_3	
OH	H	Me	(**3**)
OH	H	n-Bu	(**4**)
OH	H	Ph	(**5**)
H	Me	Me	(**6**)
H	Me	n-Bu	(**7**)
H	Me	Ph	(**8**)

Six new organotin(IV) complexes with 2,3-dihydroxybenzaldehyde-*N*(4)-methylthiosemicarbazone H_2DDMT (**1**) and 2-hydroxy-5-methylbenzaldehyde-*N*(4)-methylthiosemicarbazone H_2DMMT (**2**), [MeSnCl(DDMT)] (**3**), [BuSnCl(DDMT)] (**4**), [PhSnCl(DDMT)] (**5**), [[MeSnCl(DMMT)] (**6**), [BuSnCl(DMMT)] (**7**), and [PhSnCl(DMMT)] (**8**) have been synthesized. The ligands are coordinated to tin(IV) through the phenoxide-O, azomethine-N, and thiolate-S as a dinegative tridentate chelating agent; the coordination number of tin is five. *In vitro* cytotoxicity assays against MCF-7 cancer cell line showed that **3**–**8** possess activity.

The *N*(4)-methylthiosemicarbazone derivatives H_2DDMT (**1**) and H_2DMMT (**2**) have been prepared from the reaction of 4-methylthiosemicarbazide with 2,3-dihydroxybenzaldehyde and 2-hydroxy-5-methylbenzaldehyde, respectively. Six new organotin(IV) complexes, [MeSnCl(DDMT)] (**3**), [BuSnCl(DDMT)] (**4**), [PhSnCl(DDMT)] (**5**), [MeSnCl(DMMT)] (**6**), [BuSnCl(DMMT)] (**7**), and [PhSnCl(DMMT)] (**8**) have been synthesized by direct reaction of corresponding organotin(IV) chloride(s) with these ligands. The ligands and their compounds have been characterized by elemental analysis, molar conductivity, UV–Vis, FT-IR, and NMR (^{1}H, ^{13}C, and ^{119}Sn) spectroscopy. The molecular structures of **1** and **2** were determined by X-ray crystallography. Spectroscopic data suggested that the ligands were coordinated to tin(IV) as dinegative tridentate via phenoxide-O, azomethine-N, and thiolate-S atoms. The crystal structures revealed that the ligands exist in thione form in the solid state. *In vitro* cytotoxicity assays were carried out for all the compounds against

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MCF-7 cancer cell line. The results have shown that different organotin(IV) groups showed characteristic differences in their biological activity.

Keywords: *N*(4)-methylthiosemicarbazones; Organotin(IV) complexes; Synthesis; Characterization; Crystal structure; Cytotoxicity

1. Introduction

The synthesis and structural studies of thiosemicarbazones have shown a broad range of biological and pharmaceutical activities such as antitumor, antiviral, antitubercular, antibacterial, antihypertensive, and antimalarial [1–6]. Thiosemicarbazones have become an area of intensive study because of their biological activities and have obtained much attention [7–9]. Thiosemicarbazone derivatives with tridentate donor sites would provide the five-coordinate environment to the metal center [10–12]. Thiosemicarbazone with ONS donors have received attention in the expansion of coordination chemistry as they easily form complexes with metal ions [13–15]. Transition metal complexes of thiosemicarbazone derivatives have been broadly studied for their potential biological applications [16–19]. Moreover, biological activities of organotin(IV) complexes with thiosemicarbazones have been well established [20–22]. A variety of new substituted thiosemicarbazone derivatives are synthesized and explored for their potential biological activities. To investigate new chemical entities with potential biological properties remains a challenging objective for synthetic chemists. In the present work, we describe the synthesis, characterization, and cytotoxic activities of organotin(IV) complexes with *N*(4)-methylthiosemicarbazone derivatives derived from 2,3-dihydroxybenzaldehyde and 2-hydroxy-5-methylbenzaldehyde. X-ray crystal structures of the ligands are also described. In the present study, the ligands were coordinated to tin(IV) centers as tridentate ONS donors.

2. Experimental

2.1. *Materials and methods*

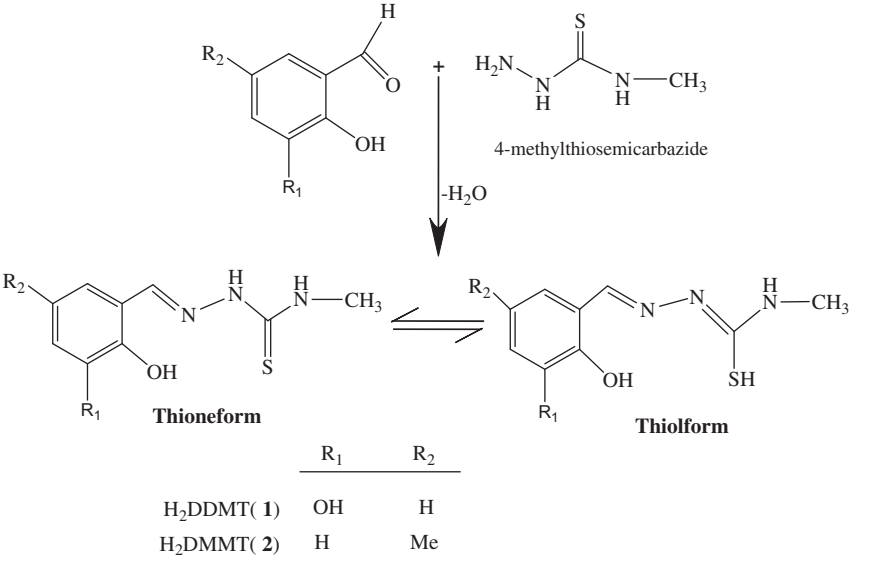
All reagents were purchased from Fluka, Aldrich, and Sigma. All solvents were received as reagent grade and used without purification. Melting point was measured by the Stuart Scientific SMP1 melting point apparatus. UV–Vis spectra were recorded in DMSO with a Perkin Elmer Lambda 25 UV–Vis spectrophotometer. Infrared (IR) spectra were recorded by the Perkin Elmer System 2000 spectrophotometer using KBr pellets from 4000–400 cm^{-1} at room temperature. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on Bruker 500 and 400 MHz NMR spectrophotometers relative to $SiMe_4$ and $SnMe_4$ in DMSO. Elemental analyses were conducted by the Perkin Elmer 2400 Series-11 CHN analyzer. Molar conductivity measurements were carried out with a Jenway 4510 conductivity meter using DMSO. X-ray crystallographic data were recorded on a Bruker SMART APEXII CCD area-detector diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 100 K. The data were collected and reduced using APEX2 and SAINT. The structures were solved using the SHELXS-97 program package, and refined using the SHELXL-97 program package. All nonhydrogen atoms were anisotropically refined. Molecular graphics were created using SHELXTL-97.

2.2. *Synthesis of 2,3-dihydroxybenzaldehyde-*N*(4)-methylthiosemicarbazone H_2DDMT (1)*

A solution of 2,3-dihydroxybenzaldehyde (0.55 g, 4.0 mmol) in ethanol (20 mL) was added to a solution of 4-methylthiosemicarbazide (0.42 g, 4.0 mmol) in ethanol (20 mL). The resulting pink solution was refluxed with stirring for 2 h (scheme 1). A white fluffy product formed when the solution cooled down to room temperature, was then filtered, washed with ethanol, and air dried. M.p.: 204–206 °C, (0.81 g, 83%). UV–Vis (DMSO) $\lambda_{max/nm}$: 263, 329, 364: FT-IR (KBr, cm^{-1}) ν_{max}: 3451 (s, OH), 3147 (m, NH), 1610 (m, C=N), 1546 (s, C_{aro}–O), 995 (w, N–N), 1367, 865 (s, C–S). ^{1}H NMR (DMSO-d_6, ppm): 11.39 (s, 1H, N2–H), 10.14, 10.55 (s, 1H, s, 1H, OH), 9.85 (m, 1H, N3–H), 8.40 (s, 1H, C7–H), 7.43 (d, 1H, J = 7.8, aroC4–H), 7.26 (d, 1H, J = 8.1, aroC6–H), 7.04 (t, 1H, aroC5–H), 3.01 (d, 3H, C9–H). ^{13}C NMR (DMSO-d_6, ppm): 190.45 (C=S), 155.54 (C=N), 145.12–116.32 (aromatic–C), 30.62 (CH_3). Anal. Calcd for $C_9H_{11}N_3O_2S$: C, 47.94; H, 4.88; N, 18.64. Found: C, 48.00; H, 4.68; N, 18.52%.

2.3. *Synthesis of 2-hydroxy-5-methylbenzaldehyde-*N*(4)-methylthiosemicarbazone H_2DMMT (2)*

H_2DMMT (**2**) was synthesized as described for **1** from 2-hydroxy-5-methylbenzaldehyde (0.54 g, 4.0 mmol) (scheme 1) and the product was formed as white microcrystals. M.p.: 217–219 °C, (0.75 g, 77%). UV–Vis (DMSO) $\lambda_{max/nm}$: 266, 324, 368: FT-IR (KBr, cm^{-1}) ν_{max}: 3358 (s, OH), 3145 (m, NH), 1603 (m, C=N), 1556 (s, C_{aro}–O), 1005 (w, N–N), 1376, 856 (m, C–S). ^{1}H NMR (DMSO-d_6, ppm): 11.35 (s, 1H, N2–H), 10.71 (s, OH), 9.38 (m, 1H, N3–H), 8.33 (s, 1H, C7–H), 7.72 (d, 1H, J = 7.1, aroC3–H), 7.02 (s, 1H, aroC6–H), 6.76 (d, 1H, J = 7.4, aroC4–H), 3.02 (d, 3H, C9–H), 2.22 (s, 3H, H_3C–Ph). ^{13}C NMR (DMSO-d_6, ppm): 187.41 (C=S), 154.18 (C=N), 140.01–115.90 (aromatic–C), 30.63 (CH_3),



	R_1	R_2
H_2DDMT(**1**)	OH	H
H_2DMMT(**2**)	H	Me

Scheme 1. Synthesis of H_2DDMT (**1**) and H_2DMMT (**2**).

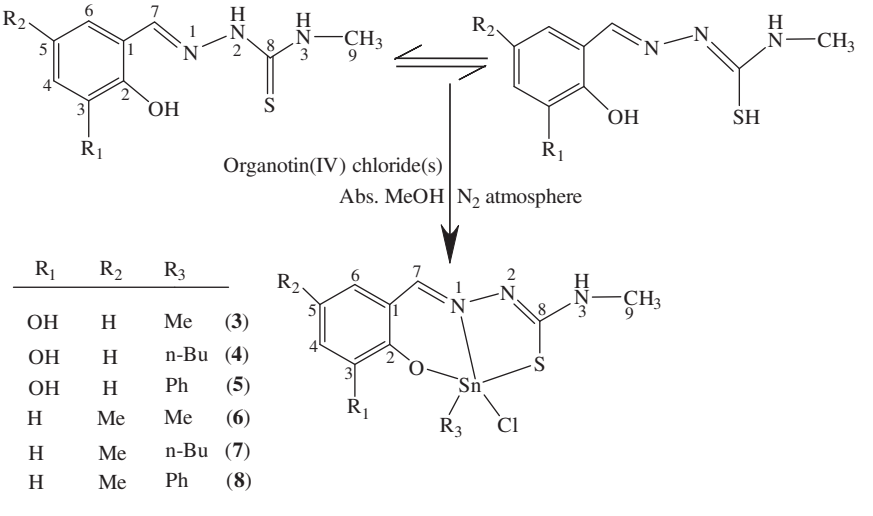
20.04 (CH_3–Ph). Anal. Calcd for $C_{10}H_{13}N_3OS$: C, 53.73; H, 5.82; N, 18.80. Found: C, 53.29; H, 5.84; N, 18.99%.

2.4. *Synthesis of [MeSnCl(DDMT)] (3)*

H_2DDMT (**1**) (0.381 g, 1.0 mmol) was dissolved in absolute methanol (10 mL) under a nitrogen atmosphere in a round-bottomed reaction flask. Then, a methanolic solution of methyltin(IV) trichloride (0.24 g, 1.0 mmol) was added dropwise and resulted in a yellow solution. The resulting reaction mixture was refluxed for 4 h (scheme 2) and cooled to room temperature. Yellow microcrystals were obtained from slow evaporation of the resulting solution at room temperature. The microcrystals were filtered off, washed with a small amount of cold methanol, and dried in *vacuo* over silica gel. M.p.: 245–247 °C, (0.46 g, 74%). Molar conductance (DMSO) $\Omega^{-1}cm^2\ mol^{-1}$: 10.45: UV–Vis (DMSO) $\lambda_{max/nm}$: 266, 345, 367, 425: FT-IR (KBr, cm^{-1}) ν_{max}: 3243 (s, OH), 3110 (m, NH), 1580 (m, C=N–N=C), 1529 (s, C_{aro}–O), 1027 (w, N–N), 1327, 845 (m, C–S), 595 (w, Sn–C), 556 (w, Sn–O), 472 (w, Sn–N). ^{1}H NMR (DMSO-d_6, ppm, $^2J[^{119}Sn, ^1H]$): 10.12 (s,1H, OH), 9.80 (m, 1H, N3–H), 8.37 (s, 1H, C7–H), 7.55 (d, 1H, $J = 7.5$, aroC4–H), 7.32 (d, 1H, $J = 7.9$, aroC6–H), 7.08 (t, 1H, aroC5–H), 3.05 (d, 3H, C9–H), 1.14 (s, 3H, Sn–CH_3, [82.47 Hz]). ^{13}C NMR (DMSO-d_6, ppm): 180.23 (C=S), 165.82 (C=N), 148.22–130.11 (aromatic–C), 31.18 (CH_3), 16.22 (Sn–CH_3). ^{119}Sn NMR (DMSO-d_6) δ: −162.32. Anal. Calcd for $C_{10}H_{12}ClN_3O_2SSn$: C, 30.61; H, 3.08; N, 10.71. Found: C, 30.55; H, 3.01; N, 10.62%. Complexes **4** and **5** were synthesized using a similar procedure to **3** using appropriate organotin(IV) chloride(s) (scheme 2).

2.5. *Synthesis of [BuSnCl(DDMT)] (4)*

M.p.: 255–257 °C, (0.51 g, 77%). Molar conductance (DMSO) $\Omega^{-1}cm^2\ mol^{-1}$: 13.31: UV–Vis (DMSO) $\lambda_{max/nm}$: 260, 340, 360, 421: FT-IR (KBr, cm^{-1}) ν_{max}: 3314 (s, OH), 3122



R_1	R_2	R_3	
OH	H	Me	(**3**)
OH	H	n-Bu	(**4**)
OH	H	Ph	(**5**)
H	Me	Me	(**6**)
H	Me	n-Bu	(**7**)
H	Me	Ph	(**8**)

Scheme 2. Synthesis of organotin(IV) complexes **3–8**.

(m, NH), 1583(m, C=N–N=C), 1520 (s, C_{aro}–O), 1025 (w, N–N), 1322, 837 (m, C–S), 599 (w, Sn–C), 550 (w, Sn–O), 464 (w, Sn–N). ^{1}H NMR (DMSO-d_6, ppm): 10.08 (s,1H, OH), 9.82 (m, 1H, N3–H), 8.34 (s, 1H, C7–H), 7.45 (d, 1H, J = 7.1, aroC4–H), 7.30 (d, 1H, J = 7.6, aroC6–H), 7.06 (t, 1H, aroC5–H), 3.11 (d, 3H, C9–H), 1.50–1.54 (t, 2H, Sn–$\underline{CH_2}$–CH_2–CH_2–CH_3), 1.45–1.49 (m, 2H, Sn–CH_2–$\underline{CH_2}$–CH_2–CH_3), 1.38–1.41 (m, 2H, Sn–CH_2–CH_2–$\underline{CH_2}$–CH_3), 0.96–0.99 (t, 3H, Sn–CH_2–CH_2–CH_2–$\underline{CH_3}$). ^{13}C NMR (DMSO-d_6, ppm): 178.45 (C=S), 163.20 (C=N), 151.35–131.23 (aromatic–C), 30.88 (CH_3), 24.11, 22.80, 20.75, 18.54 (Sn–CH_2–CH_2–CH_2–CH_3). ^{119}Sn NMR (DMSO-d_6) δ: −168.45. Anal. Calcd for $C_{13}H_{18}ClN_3O_2SSn$: C, 35.93; H, 4.18; N, 9.67. Found: C, 35.99; H, 4.25; N, 9.75%.

2.6. *Synthesis of [PhSnCl(DDMT)] (5)*

M.p.: 239–241 °C, (0.54 g, 79%). Molar conductance (DMSO) $\Omega^{-1}cm^2\ mol^{-1}$: 12.11: UV–Vis (DMSO) $\lambda_{max/nm}$: 239, 335, 381, 427: FT-IR (KBr, cm^{-1}) ν_{max}: 3355 (m, OH), 3135 (m, NH), 1585 (m, C=N–N=C), 1505 (s, C_{aro}–O), 1020 (w, N–N), 1333, 841 (m, C–S), 593 (w, Sn–C), 543 (w, Sn–O), 464 (w, Sn–N). ^{1}H NMR (DMSO-d_6, ppm): 10.10 (s, 1H, OH), 9.81 (m, 1H, N3–H), 8.30 (s, 1H, C7–H), 7.51–7.07(m, 8H, aro–H), 3.09 (d, 3H, C9–H). ^{13}C NMR (DMSO-d_6, ppm): 177.88 (C=S), 160.22 (C=N), 152.45–133.45 (aromatic–C), 30.98 (CH_3). ^{119}Sn NMR (DMSO-d_6) δ: −178.15. Anal. Calcd for $C_{15}H_{14}ClN_3O_2SSn$: C, 39.64; H, 3.10; N, 9.25. Found: C, 39.55; H, 3.15; N, 9.36%.

2.7. *Synthesis of [MeSnCl(DMMT)] (6)*

H_2DMMT (**2**) (0.223 g, 1.0 mmol) was dissolved in absolute methanol (10 mL) under a nitrogen atmosphere in a round-bottomed reaction flask. Then, a methanolic solution of methyltin(IV) trichloride (0.24 g, 1.0 mmol) was added dropwise and resulted in a yellow solution. The resulting reaction mixture was refluxed for 4 h (scheme 2) and cooled to room temperature. The yellow microcrystals were filtered off, washed with a small amount of cold methanol, and dried in *vacuo* over silica gel. M.p.: 265–267 °C, (0.35 g, 76%). Molar conductance (DMSO) $\Omega^{-1}cm^2\ mol^{-1}$: 8.33: UV–Vis (DMSO)$\lambda_{max/nm}$: 273, 325, 371, 508: FT-IR (KBr, cm^{-1}) ν_{max}: 3215 (s, NH), 1575 (m, C=N–N=C), 1515 (s, C_{aro}–O), 1035 (w, N–N), 1320, 830 (m, C–S), 587 (w, Sn–C), 551 (w, Sn–O), 447 (w, Sn–N). ^{1}H NMR (DMSO-d_6, ppm, ^2J[^{119}Sn, ^{1}H]): 9.45 (m, 1H, N3–H), 8.25 (s, 1H, C7–H), 7.80 (d, 1H, J = 7.2, aroC3–H), 7.11 (s, 1H, aroC6–H), 6.85 (d, 1H, J = 7.8, aroC4–H), 3.08 (d, 3H, C9–H), 2.25 (s, 3H, H_3C–Ph), 1.18 (s, 3H, Sn–CH_3, [78.42 Hz]). ^{13}C NMR (DMSO-d_6, ppm): 175.72 (C=S), 168.23 (C=N), 150.33–135.18 (aromatic–C), 31.89 (CH_3), 21.12 (CH_3–Ph), 17.11 (Sn–CH_3). ^{119}Sn NMR (DMSO-d_6,) δ: −174.22. Anal. Calcd for $C_{11}H_{14}ClN_3OSSn$: C, 33.84; H, 3.61; N, 10.76. Found: C, 33.95; H, 3.71; N, 10.84%.

Complexes **7** and **8** were synthesized using a similar procedure to **6** using corresponding organotin(IV) chloride(s) (scheme 2).

2.8. *Synthesis of [BuSnCl(DMMT)] (7)*

M.p.: 260–262 °C, (0.41 g, 81%). Molar conductance (DMSO) $\Omega^{-1}cm^2\ mol^{-1}$: 11.38: UV–Vis (DMSO) $\lambda_{max/nm}$: 270, 327, 375, 405: FT-IR (KBr, cm^{-1}) ν_{max}: 3201 (s, NH), 1578 (m, C=N–N=C), 1518 (s, C_{aro}–O), 1030 (w, N–N), 11,315, 832 (m, C–S), 589 (w, Sn–C),

555 (w, Sn–O), 444 (w, Sn–N). ^{1}H NMR (DMSO-d_6, ppm): 9.48 (m, 1H, N3–H), 8.20 (s, 1H, C7–H), 7.77 (d, 1H, $J = 7.6$, aroC3–H), 7.08 (s, 1H, aroC6–H), 6.83 (d, 1H, $J = 7.7$, aroC4–H), 3.07 (d, 3H, C9–H), 2.23 (s, 3H, H_3C–Ph), 1.62–1.56 (t, 2H, Sn–$\underline{CH_2}$–CH_2–CH_2–CH_3), 1.51–1.48 (m, 2H, Sn–CH_2–$\underline{CH_2}$–CH_2–CH_3), 1.38–1.30 (m, 2H, Sn–CH_2–CH_2–$\underline{CH_2}$–CH_3), 0.99–0.91 (t, 3H, Sn–CH_2–CH_2–CH_2–$\underline{CH_3}$). ^{13}C NMR (DMSO-d_6, ppm): 173.30 (C=S), 167.42 (C=N), 148.44–134.06 (aromatic–C), 30.85 (CH_3), 20.50 (CH_3–Ph), 25.32, 23.92, 21.45, 18.25 (Sn–CH_2–CH_2–CH_2–CH_3). ^{119}Sn NMR (DMSO-d_6) δ: −174.22. Anal. Calcd for $C_{14}H_{20}ClN_3OSSn$: C, 38.87; H, 4.66; N, 9.71. Found: C, 38.94; H, 4.60; N, 9.82%.

2.9. *Synthesis of [PhSnCl(DMMT)] (8)*

M.p.: 258–260 °C, (0.41 g, 78%). Molar conductance (DMSO) $\Omega^{-1}cm^2\ mol^{-1}$: 9.45: UV–Vis (DMSO) $\lambda_{max/nm}$: 268, 325, 369, 410: FT-IR (KBr, cm^{-1}) ν_{max}: 3210 (m, NH), 1570 (m, C=N–N=C), 1510 (s, C_{aro}–O), 1022 (w, N–N), 1319, 836 (m, C–S), 586 (w, Sn–C), 545 (w, Sn–O), 482 (w, Sn–N). ^{1}H NMR (DMSO-d_6, ppm): 9.48 (m, 1H, N3–H), 8.21 (s, 1H, C7–H), 7.62–7.10 (m, 8H, aromatic–H), 3.04 (d, 3H, C9–H), 2.26 (s, 3H, H_3C–Ph). ^{13}C NMR (DMSO-d_6, ppm): 170.88 (C=S), 165.72 (C=N), 149.55–130.25 (aromatic–C), 30.90 (CH_3), 20.75 (CH_3–Ph). ^{119}Sn NMR (DMSO-d_6,) δ:− 171.55. Anal. Calcd for $C_{16}H_{16}ClN_3OSSn$: C, 42.47; H, 3.56; N, 9.21. Found: C, 42.40; H, 3.51; N, 9.33%.

2.10. *Cytotoxic effect evaluation by MTT assays*

The cytotoxic effects of **1–8** toward human breast cancer cell lines (MCF-7) were evaluated with MTT assay procedures [23]. MCF-7 cells (1.5×10^5 cells mL^{-1}, 100 µL $well^{-1}$) were seeded in a 96-well microtiter plate. The plate was incubated in a CO_2 incubator overnight to allow cell attachment. After 24 h from seeding, the cells were incubated with 100 µL of test organotin(IV) complexes into each well containing the cells. The test compounds were diluted with media into the various concentrations from the stock. The plates were incubated at 37 °C with an internal atmosphere of 5% CO_2 for 3 days. Then, 20 µL of MTT reagent was added into each well and the plates were incubated for 4 h. After this incubation period, 50 µL of MTT lysis solution (DMSO) was added into the wells. The plates were further incubated for 5 min in a CO_2 incubator. Finally, the absorbance was measured at 570 nm with the use of a standard ELISA microplate reader. Data were recorded and analyzed to assess the effects of test compound on cell viability. The drug concentration required to reduce cell number to 50% of controls following a 72-h continuous drug exposure (IC_{50}) was obtained from semilogarithmic dose–response plots. The medium without samples served as control and all tests were performed in triplicate.

3. Results and discussion

3.1. *Synthesis*

H_2DDMT (**1**) and H_2DMMT (**2**) were synthesized by condensation of thiosemicarbazide with salicylaldehyde derivatives [24]. Both ligands have two possible tautomers, thione or thiol forms (scheme 1). New organotin(IV) complexes were synthesized by reaction of

organotin(IV) chloride(s) with *N*(4)-methylthiosemicarbazone ligands. All the compounds were obtained in good yields (73–84%). The physical properties and analytical data of the compounds are given in the experimental section. All compounds are yellow solids, stable in air, and soluble in solvents such as MeOH, $CHCl_3$, CH_2Cl_2, DMSO, DMF, and THF. The molar conductivities of the complexes were 13.31–8.33 Ω^{-1} cm^2 mol^{-1} in DMSO, which evidences the neutral behavior of the organotin(IV) complexes [25].

3.2. *UV–Visible spectra*

Electronic spectra of the free ligands exhibited three bands from 266 to 263, 329 to 324, and 364 to 368 nm corresponding to the intraligand n–π* transition of the azomethine and π–π* transitions of the aromatic ring and thiolate [26]. After complexation, the bands shifted to higher energy in the spectra of complexes due to intraligand transition. A new absorption in the complexes at 427–405 nm was assigned to ligand → metal charge transfer band [27].

3.3. *Infrared spectra*

IR bands most useful to ascertain the mode of coordination of the ligands are *ν*(C=N), *ν*(C_{aro}–O), *ν*(N–N), and *ν*(C–S). IR spectra of uncoordinated phenolic OH and hydrazinic NH show strong bands at 3355–3243 and 3135–3110 cm^{-1}, respectively. The spectra *ν*(OH) and *ν*(NH) bands disappeared completely after complexation showing deprotonation of the ligands during coordination to tin(IV). The absence of the *ν*(S–H), stretch around 2700 cm^{-1} indicates that the ligands remain in thione form in the solid state [28, 29]. The bands corresponding to newly formed *ν*(C=N–N=C) shifted to lower frequencies in all the complexes compared to the free ligands, a clear indication of coordination via azomethine nitrogen [30]. The lowering of *ν*(C_{aro}–O) in the complexes compared to the free ligands further confirmed coordination with phenolic oxygen to tin(IV). The increase in the frequency of *ν*(N–N) in spectra of complexes due to increase in the bond strength, again confirms coordination through the azomethine nitrogen. The stretching and bending vibrations of *ν*(C–S) at a lower frequency in all the complexes suggest coordination of tin(IV) through sulfur [31]. The appearance of three new bands at 599–586, 556–543, and 472–442 cm^{-1} in all complexes gives evidence for the presence of *ν*(Sn–C), *ν*(Sn–O), and *ν*(Sn–N), respectively.

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

The ^{1}H NMR spectral assignments of ligands and organotin(IV) complexes were carried out based on the atom labeling in scheme 2. The appearance of sharp singlet at 10.55–10.71 ppm in spectra of the free ligands assigned to the phenolic–OH proton fully disappeared in spectra of all organotin(IV) complexes, indicating the participation of phenolic oxygen in coordination. The absence of N2–H signal in spectra of **3–8** suggests deprotonation and coordination of thionic form of the ligand to tin(IV). The chemical shift of the terminal N3–H appeared almost in the same region for ligands and **3–8**. In all complexes, proton signal of C7–H shifted downfield with respect to the free ligands, confirming coordination of the azomethine nitrogen to the tin(IV). The proton signals of aromatic ring of the ligands and their complexes were observed at 7.02–7.80 ppm. A doublet was

observed at 3.02–3.11 ppm due to C9–H of the ligands and their complexes. The ($-CH_3$) group attached to the phenyl ring in **1** and **3–5** is a singlet at 2.22–2.26 ppm. In **3** and **6**, the peak at 1.14 and 1.18 ppm is due to methyl attached to tin(IV). The ^2J [^{119}Sn, ^{1}H] coupling satellites of **3** and **6** of 80.47 and 78.42 Hz, respectively, confirmed five-coordinate tin (IV) [32].

^{13}C NMR spectra of all compounds also supported proposed structures. The carbon signal of the (C=S) group shifted upfield in the **3–5** with respect to free ligands, confirming coordination of the N=C–S with Sn(IV). The chemical shifts of carbon in (C=N) downfield in all the complexes compared to free ligands clearly indicated the azomethine nitrogen coordinated to Sn(IV). Signals corresponding to the aromatic carbons downfield compared to **1**, suggested phenolic ring oxygen is coordinated to Sn(IV). The carbon signals of ($N-CH_3$) were observed in expected region for ligands and their complexes.

^{119}Sn NMR spectra of **3–8** showed a single signal confirming the formation of single species. ^{119}Sn chemical shifts of **3–8** from −162.32 to −178.15 ppm indicated coordination number of the Sn is five in solution [33, 34].

3.5. *Crystal structure of H_2DDMT (1)*

Suitable single crystals of H_2DDMT (**1**) were grown from methanol at room temperature. The molecular structure of H_2DDMT (**1**) along with the atom numbering scheme and its packing in the crystal lattice are given in figures 1 and 2, respectively. Table 1 summarizes crystal data and structure refinement results of **1**. Selected bond lengths (Å) and angles (°) are shown in table 2. The compound crystallizes in a triclinic lattice with space group *P-1*. According to the crystal structure, **1** exists in the thione form with S1 and N1 in the E configuration with respect to the N2–C8 bond. This is confirmed by the torsion angle of 179.40 (12)° of the N1–N2–C8–S1 [35]. In **1**, the –C=N–N–C– chain bridging the methylimino group and the benzene ring adopts an extended conformation with a C7–N1–N2–C8 torsion angle of 169.99 (16)°. The thione form in the solid state is strongly confirmed by the observed bond distances C8–S1 [1.6742(17) Å] and C8–N2 [1.360(2) Å]. The C8–S1 distance of 1.6742(17) Å is closer to the C=S bond distance [1.60 Å] [36] than to the C–S bond distance [1.81 Å]. The C8–N2 distance of 1.360(2) Å is in the range of other

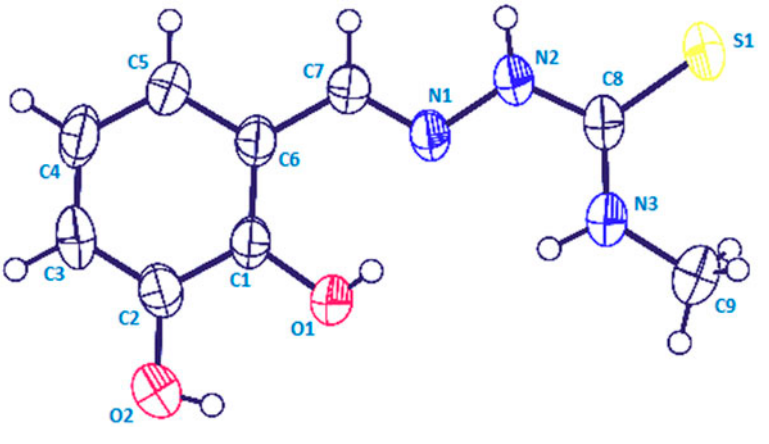


Figure 1. Molecular structure of 2,3-dihydroxybenzaldehyde-*N*(4)-methylthiosemicarbazone H_2DDMT (**1**).

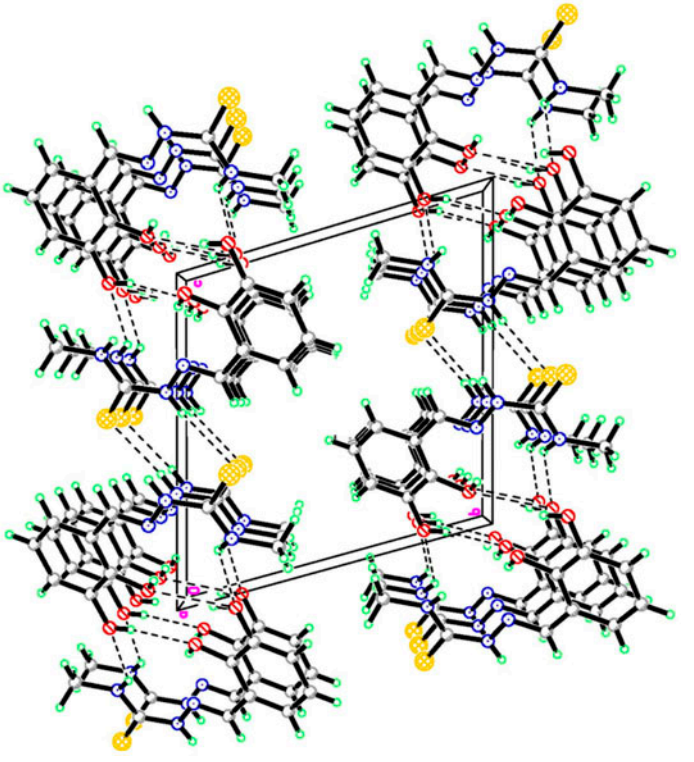


Figure 2. Crystal packing structure for **1**, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

thiosemicarbazones having C–N single bond reported previously [37–39]. The C7–N1 distance (1.279(2) Å) is nearly the same as that of the C=N double bond (1.28 Å) [40]. These bond distances are in strong support of the existence of 2,3-dihydroxybenzaldehyde-*N*(4)-methylthiosemicarbazone in the thione form in the solid state. The planarity of this section of the molecule is aided by a weak intramolecular N3H···N1 interaction. The two N-bound hydrogens are *anti*, and within the molecule, both the O1- and N3-bound hydrogens form intramolecular hydrogen bonds to the *imine*-N1. With the N1–N2–C8–S1 torsion angle of 179.(12)°, the twist about the C8–N2 bond in the *P-1* form. However, the dihedral angle between the N_3CS residue and benzene ring of 23.3(9)° is a little wider in the Cc form as the terminal methyl is slightly twisted out of the CN_3S plane: the C9–N3–C8–S1 torsion angle is −6.0(3)° to 1.5 (3)° in the *P-1* form. In the crystal packing of the *P-1* form, the molecule is stabilized by intra and intermolecular hydrogen bonding interactions (figure 2). Here, the inner N2–H2n forms a hydrogen bond to a translationally related inner O1, and the bifurcated S1 accepts hydrogen bonds from the outer, centrosymmetically related O2–H2o and a translationally related, outer N3–H1n.

3.6. *Crystal structure of H_2DMMT (2)*

Slow evaporation of **2** in methanol yielded single crystals suitable for X-ray analysis. The molecular structure of **2** along with the atom numbering scheme and its packing in the

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

Compounds	H_2DDMT(**1**)	H_2DMMT(**2**)
Empirical formula	$C_9H_{11}N_3O_2S$	$C_{10}H_{13}N_3OS$
Formula weight	225.27	223.29
Temperature (K)	297(2)	297(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
Unit cell dimensions		
a (Å)	4.6643(5)	6.1405(8)
b (Å)	10.7513(10)	13.1312(16)
c (Å)	10.9990(11)	13.9049(18)
α (°)	73.8361(19)	94.066(3)
β (°)	88.5450(18)	92.357(3)
γ (°)	80.1693(17)	99.071(2)
Volume (Å^3)	521.84(9)	1102.8(2)
Z	2	4
Calculated density (mg/m^3)	1.434	1.345
Radiation type *λ* (Å)	MoK\a	MoK\a
F(0 0 0)	236	472
Crystal size (mm)	0.548 × 0.206 × 0.051	0.447 × 0.408 × 0.063
Crystal color	Brown	Colorless
Scan range *θ* (°)	1.928–27.682	2.94–28.15
Absorption coefficient (μ) (mm^{-1})	0.294	0.271
Max. and min. transm	0.856 and 0.985	0.889 and 0.983
Goodness-of-fit on F^2	1.155	1.052
Data/restrains/parameters	2413/0/153	5800/0/299
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0400$, $wR_2 = 0.1249$	$R_1 = 0.0539$, $wR_2 = 0.1666$
R indices (all data)	$R_1 = 0.0535$, $wR_2 = 0.1452$	$R_1 = 0.0784$, $wR_2 = 0.1842$

crystal lattice are given in figures 3 and 4, respectively. Table 1 summarizes crystal data and structure refinement results of **2**. Selected bond distances (Å) and angles (°) are shown in table 2. H_2DMMT crystallizes with two molecules per asymmetric unit into a triclinic crystal system with space group of *P-I*. From data in table 2, it is clear that the two molecules in the asymmetric unit are almost identical. So the explanation will be limited to one of the molecules. **2** adopts an E configuration with respect to the C=N bond, existing in the thione form with S1A and N1A in the E configuration with respect to N2A–C8A. A torsion angle of −163 corresponding to the N3A–N2A–C8A–S1A moiety confirms the *trans* configuration of the thiocarbonyl S1A with respect to the imine nitrogen N1A [35]. The existence of 2-hydroxy-5-methylbenzaldehyde-*N*(4)-methylthiosemicarbazone **2** in the thione form in the solid state is strongly confirmed by the observed bond distances C8A–S1A (1.677 Å) close to that expected of a C=S double bond (1.60 Å) [36] and the C7A–N1A bond distance (1.287 Å) is nearly the same as that of the C=N double bond (1.28 Å) [40]. Similarly, the N1A–N2A bond distance (1.379 Å) is closer to single bond distance (1.45 Å) than to double bond distance (1.25 Å) [36]. **2** can be separated in two planar fragments that are connected by a single N1A–N2A bond. The N-methylthioureide plane includes N2A, S1A, N3A, C8A, and C9A, whereas the salicylaldimine plane includes N1A, O1A, and C5A–C7A. Dihedral angle between these two planes is 8.59(17)°. This coupled with the observation that the methyl substituent is coplanar with the benzene ring to which it is attached, the C10A–C4A–C3A–C2A torsion angle is −178.4(3)°, indicating that the molecule is approximately planar. In the crystal lattice, the packing of the molecules is stabilized by intra and intermolecular hydrogen bonding interactions. The amine-N–H3A and imine-N1A are directed to the same side of the molecule enabling the formation of an

Table 2. Selected bond lengths (Å) and angles (°) of **1** and **2**.

H_2DDMT(**1**)		H_2DMMT(**2**)	
Bond lengths (Å)			
S1–C8	1.674(17)	S1A–C8A	1.677(2)
O1–C1	1.364(2)	O1A–C1A	1.370(3)
O2–C2	1.368(2)	N1A–C7A	1.287(3)
N1–C7	1.279(2)	N1A–N2A	1.379(2)
N1–N2	1.370(19)	N2A–C8A	1.362(3)
N2–C8	1.360(2)	N3A–C8A	1.320(3)
N3–C8	1.328(2)	N3A–C9A	1.450(3)
N3–C9	1.447(2)	S1B–C8B	1.676(2)
C1–C6	1.391(2)	O1B–C1B	1.369(2)
C2–C3	1.370(3)	N1B–C7B	1.285(3)
C3–C4	1.384(3)	N1B–N2B	1.378(2)
C6–C7	1.450(2)	N2B–C8B	1.357(3)
		N3B–C8B	1.318(3)
Bond angles (°)			
C7–N1–N2	116.89(14)	C7A–N1A–N2A	114.39(17)
C8–N2–N1	120.80(15)	C8A–N2A–N1A	121.40(19)
C8–N3–C9	124.11(17)	C8A–N3A–C9A	123.9(2)
O1–C1–C6	122.64(15)	O1A–C1A–C2A	117.98(19)
O1–C1–C2	116.58(16)	O1A–C1A–C6A	121.70(18
C6–C1–C2	120.77(15)	N1A–C7A–C6A	123.69(19)
O2–C2–C3	120.09(17)	N3A–C8A–S1A	125.11(17)
O2–C2–C1	120.04(17)	N2A–C8A–S1A	117.76(17)
N3–C8–S1	123.56(13)	C7B–N1B–N2B	114.52(17)
N2–C8–S1	119.12(13)	C8B–N2B–N1B	122.19(19)
N3–C8–N2	117.32(16)	C8B–N3B–C9B	123.7(2)
		O1B–C1B–C2B	118.3(2)
		N1B–C7B–C6B	123.34(18)
		N3B–C8B–S1B	124.66(17)

intramolecular N–H···N hydrogen bond. The crystal packing is dominated by N–H···S hydrogen bonds that lead to centrosymmetric dimers. The almost co-planarity of the central atoms is ascribed to the formation of an intramolecular hydroxyl-*O*–*H*···*N*-imine hydrogen bond. These hydrogen bonds allow **2** molecules to stack along the *c*–axis and thus stabilize the packing crystal structure. Moreover, the orientation of the phenyl ring [torsion angle C1A–C6A–C7A–N1A = 2.8(3)°] is stabilized by the O1A–H1A···N1A hydrogen bond, and the *syn* conformation of C9A with respect to the S1A [torsion angle C9A–N3A–C8A–S1A = −5.5(5)°] is stabilized by the C9A–H9A···S1A and N3A–H1A···N1A hydrogen bonds. Additional stabilization is provided by C–H…π and π….π [ring centroid(hydroxybenzene)] interactions.

3.7. *Cytotoxic activity*

The cytotoxic activity of newly synthesized ligands **1** and **2** and their complexes (**3–8**) were investigated against human breast cancer cell line (MCF-7). The IC_{50} values of complexes and standard are given in table 3. The organotin(IV) complexes (**3–8**) showed more activity than the standard drug, 5-fluorouracil. Complexes **3–8** exhibit more cytotoxic effects than the parent ligands. Cytotoxic activity of **5** (IC_{50} = 4.65 μM) and **8** (IC_{50} = 3.99 μM) is more than the other complexes and much better than standard drug (IC_{50} = 7.58 μM). The higher

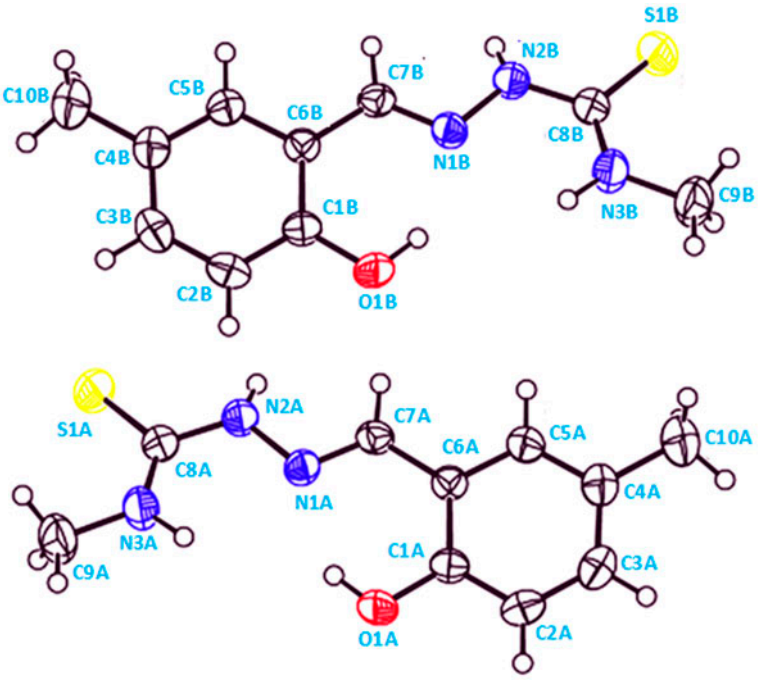


Figure 3. Molecular structure of 2-hydroxy-5-methylbenzaldehyde-*N*(4)-methylthiosemicarbazone H_2DMMT (**2**).

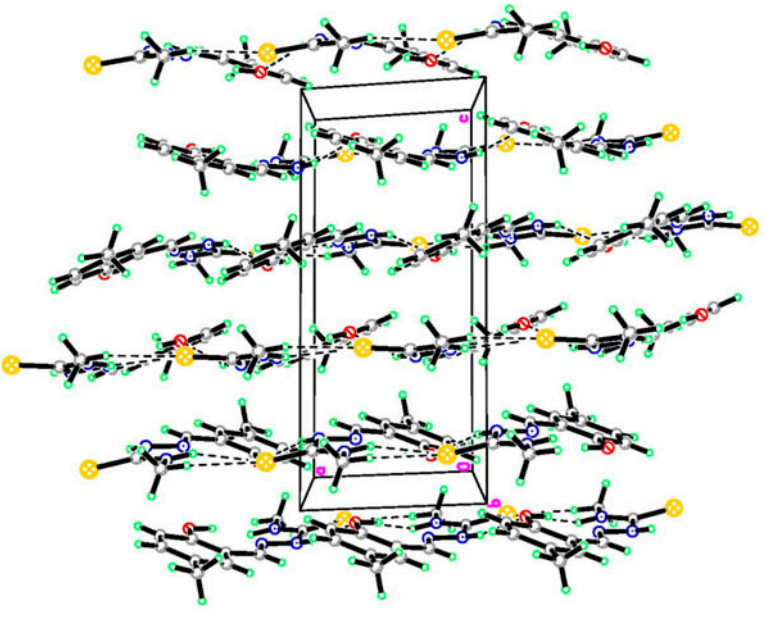


Figure 4. Crystal packing structure for **2**, viewed along the *c* axis. Hydrogen bonds are shown as dashed lines.

Table 3. Cytotoxic effect (IC_{50}, μM) of **1** and **2** and their organotin(IV) compounds (**3–8**) toward human breast cancer cell line (MCF-7).

No.	Compound	IC_{50} (μM)
1	H_2DDMT	6.47
2	H_2DMMT	6.81
3	[MeSnCl(DDMT)]	5.73
4	[BuSnCl(DDMT)]	6.82
5	[PhSnCl(DDMT)]	4.65
6	[MeSnCl(DMMT)]	5.35
7	[BuSnCl(DMMT)]	6.47
8	[PhSnCl(DMMT)]	3.99
R	5-fluorouracil	7.58

cytotoxic activity for these complexes might be due to the presence of bulky phenyl group attached to tin(IV), which facilitate binding to biological molecules by π-interactions. The better activity of methyltin(IV) complexes **3** and **6** can be explained on the basis of their high diffusion ((low molecular weights) [41]. That **3–8** exhibited higher cytotoxicity can be explained on the basis of high lipophilic nature. Cytotoxic activities of **3–8** may be due to the presence of OH/NH group to form hydrogen bonds with DNA bases. The activities of all organotin(IV) compounds are comparable with recently reported organotin complexes [42–45]. The above biological study suggests that the activity is mainly influenced by the type of organic groups on tin, diffusion, lipophilic, and steric effects [46]. By comparing the cytotoxicities with that of the standard 5-fluorouracil, it has been found that the complexes exhibited excellent activity against MCF-7 cancer cell lines.

4. Conclusion

Substituted *N*(4)-methylthiosemicarbazone and their corresponding organotin(IV) complexes have been synthesized and fully characterized. The molecular structures of **1** and **2** have been determined by single crystal X-ray diffraction. Both ligands exist in thione form in the solid state. All complexes exhibited that *N*(4)-methylthiosemicarbazone ligands coordinate to tin(IV) as dinegative tridentate ONS donors. The cytotoxic activities of the complexes against MCF-7 cell line revealed that all the complexes exhibited higher activities than 5-fluorouracil and parent ligands. Among the six complexes, phenyltin(IV) complexes **5** and **8** exhibited higher cytotoxicity.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplementary data

CCDC reference number 1019985 and 1019984 contains the supplementary crystallographic data for H_2DDMT (**1**) and H_2DMMT (**2**). This data can be obtained free of charge from the Cambridge Crystallographic data center via www.ccdc.ac.uk/data_request/cif or from the Cambridge Crystallographic data center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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