Polish J. Chem., **78**, 753–760 (2004) **INORGANIC CHEMISTRY**

Synthesis and Crystal Structure of Five-Coordinated Triorganotin Complexes with 2,5-Dimercapto-4-phenyl-1,3,4-thiodiazole

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Reactions between triorganotin chloride and 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole gave complexes $R_3Sn(S_3N_2C_8H_5)$ (**4**: R = Ph; **5**: R = $PhCH_2$ and **6**: R = *n*-Bu), respectively. All products were characterized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and two of them ((**4**) and (**5**)) have been determined by X-ray crystallography. Including the Sn–N interaction, the tin atoms of three complexes all have five-coordinated distorted trigonal bipyramidal geometry. All three complexes have antitumor activity in bioactivity measurements. Crystal data for complex (**4**): monoclinic, space group *P2(1)/c*, a = 9.696(2) Å, b = 14.773(3) Å, c = 17.466(4) Å, β = 92.599(3)°, and Z = 4. Crystal data for complex (**5**): triclinic, space group *P-1*, a = 9.744(6) Å, b = 16.338(10) Å, c = 17.957(12) Å, α = 90.000(12)°, β = 100.735(11)°, γ = 90.000(12)° and Z = 4.

Key words: organotin, 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole, crystal structure

Metal thiolato complexes have been extensively studied over a number of years, stimulated both by their coordination chemistry and their relevance in biology [1–3]. Recently, attention has been paid to the organotin heteroarenethiolates [4], because higher coordination numbers can be generated by Sn–N interactions. And it is worth to note, that there are important relations between antitumor activity and the Sn–N bond lengths [5]. In this regard, the most studied systems are triorganotin heteroarenethiolates. As shown in Scheme 1, in such complexes, the higher coordination number can arise either *via* intramolecular coordination of the tin center with the donor atoms, *e.g.*, as **1** [6] and **2** [7], or intermolecularly as in triphenyl(4-pyridinethiolato)stannane [8], or by both intra-/ inter-molecular interactions in complex **3** (R = Ph, R′ = $PHCH_2$) [9]. The geometry is usually described as distorted trigonal bipyramidal, and most of these complexes with Sn–N interactions have antitumor activity.

As the consequence of our continuing interest on organotin heteroarenethiolates [10], we investigated the reactions of 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole (dmpt) with triorganotin chloride R_3SnCl. Three complexes were obtained, $R_3Sn(S_3N_2C_8H_5)$ (**4**: R = Ph; **5**: R = $PhCH_2$ and **6**: R = *n*-Bu). All products were charac-

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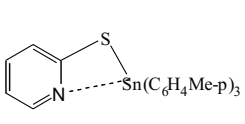
Scheme 1



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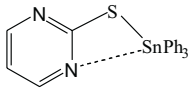

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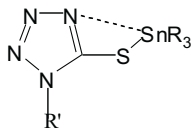

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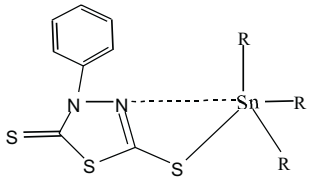

4: R = Ph; **5**: R = $PhCH_2$, **6**: R = *n*-Bu

terized by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and two of them ((**4**) and (**5**)) have been determined by X-ray crystallography.

EXPERIMENTAL

The melting points were obtained on a Kofler micro melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet-460 spectrophotometer, using KBr discs and sodium chloride optics. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer, operating at 300 and 75.3MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR. Elemental analyses were performed with a PE-2400 II elemental analyser.

Preparation of complex (4): A mixture of Kdmpt (0.53 g, 2 mmol) and Ph_3SnCl (0.760 g, 2 mmol) in benzene (20 mL) in a Schlenk flask was stirred for 12 h at 40°C, cooled to room temperature and filtered. The filtered solution was gradually removed by evaporation under vacuum until a solid product was obtained. Colourless crystals of complex **4** were recrystallized from ether-dichloromethane. Yield 89%. m.p. 138–140°C. Anal. calcd. for $C_{26}H_{20}N_2S_3Sn$ (FW: 575.37): C, 54.28; H, 3.50; N, 4.87. Found: C, 54.25; H, 3.51; N, 4.85%. ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 6.67~7.59 (m, 20H). ^{13}C NMR ($CDCl_3$): δ 168.5 (C–S), 173.5 (C=S), 128.1 (*m*-C), 129.3 (*p*-C), 136.5 (*o*-C), 148.6 (*i*-C). IR (KBr) ν: 1591 (C=N); 1383 (C–N); 1155 (C=S); 1059 (N–N); 726 (C–S); 537 (Sn–C); 301 (Sn–S) cm^{-1}.

Preparation of complex (5): This was similarly prepared as **4** from Kdmpt (0.53 g, 2 mmol) and $(PhCH_2)_3SnCl$ (0.37 g, 1 mmol) in benzene (20 mL). Colourless crystals of complex **5** were recrystallized from dichloromethane-hexane. Yield 83%. m.p. 90–92°C. Anal. calcd. for $C_{29}H_{26}N_2S_3Sn$ (FW: 617.45): C, 56.41; H, 4.24; N, 4.54. Found: C, 56.40; H, 4.25; N, 7.53%. ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 6.67~7.59 (m, 20H), 2.68–3.26 (m, 6H). ^{13}C NMR: δ 168.4 (C–S), 173.4 (C=S), 37.5 (CH_2–Ph), 127.4 (*m*-C), 128.2 (*p*-C), 127.3 (*o*-C), 124.2 (*i*-C). IR (Kbr) ν: 1595 (C=N); 1340 (C–N); 1151 (C=S); 1058 (N–N); 725 (C-S); 537 (Sn–C); 309 (Sn–S) cm^{-1}.

Preparation of complex (6): This was similarly prepared as **4** from Kdmpt (0.53 g, 2 mmol) and $(n\text{-}Bu)_3SnCl$ (0.65 g, 2 mmol) in benzene (20 mL). Yield 85%. m.p. 46–48°C. ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 6.67~7.59 (m, 5H), 1.10~1.75 (m, 18H) and 0.90–1.10 (t, 9H); ^{13}C NMR ($CDCl_3$): δ 168.0 (C–S), 173.4 (C=S), 13.6, 26.4, 27.6, 29.7 (^{n}Bu). IR (KBr) ν: 1597 (C=N), 1346 (C–N), 1135 (C=S), 1060 (N–N), 730 (C–S), 537 (Sn–C), 309 (Sn–S) cm^{-1}. Anal. calcd. for $C_{20}H_{32}N_2S_3Sn$: C, 46.61; H, 6.26; N, 5.44. Found: C, 46.62; H, 6.25; N, 4.46.

X-ray crystallography: All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer. Semiempirical absorption correction based on equivalent reflections was applied, and the structure was solved by direct methods and refined by a full-matrix least squares procedure based on F^2 using the SHELXL-97 program system. All data were collected with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 298(2) K, using the area detector scan technique, and corrected for Lorentz and polarization effects but not for absorption, satistying $I \geq 2\sigma$ (I). The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included.

RESULTS AND DISCUSSION

The IR spectra of R_3SnCl exhibit medium intensity bands at 310–400 cm^{-1}, due to the Sn-Cl groups [11]. This band is absent in the spectra of the corresponding complexes, which shows that all chlorine atoms were substituted. But a new absorption appears at 441 cm^{-1} for **4**, 449 cm^{-1} for **5**, 445 cm^{-1} for **6**, which are located within the range for Sn–S vibration observed in common organotin derivatives of thiolate (400–500 cm^{-1}) [12–13]. The middle intensity bands observed at 1635 cm^{-1} in the spectra of complexes **4**, **5** and **6** have been assignable to ν(C=N) according to literatures [14–16]. The appearance of Sn–S and C=N absorptions suggested that the ligand coordinated to tin by sulfur atom. In the ^{13}C-NMR spectra of all six complexes **4–6**, chemical shifts are quite similar to those of the parent ligand. Only a small shift in the positions of heterocyclic carbon atom (C=S) are seen, which may be due to the deshielding of the carbon atom upon deprotonation of the thiol group and coordination through sulfur atom [17].

Biological activity: The antitumor activity tests in vitro showed that the inhibition rates (%) of **4**, **5** and **6** against culture cells of Ehrlich ascites carcinoma are 62, 67 and 73, respectively, so the complexes have higher antitumor activity to Ehrlich ascites carcinoma than *cis*-$[Pt(NH_3)_2Cl_2]$ (55). The crystal data and the most relevant experimental parameters used in the X-ray measurements and in the crystal structure analyses are reported in Table 1. Details for the two complexes are as follows. A white crystal of complex (**4**) suitable for X-ray analysis (0.30×0.25×0.10 mm) was obtained by recrystallization from dichloromethane-ether. The resolution of the structure is correct as confirmed by the acceptable R_1(F) (0.0313) and goodness-of-fit (0.927) values. A white crystal of complex (**2**) suitable for X-ray analysis (0.15×0.10×0.10 mm) was obtained by recrystallization from dichloromethane-hexane. The resolution of the structure is correct as confirmed by the acceptable R_1(F) (0.0519) and goodness-of-fit (0.787) values.

Structure of the complexes (4) and (5): The selected bond distances and angles are summarized in Table 2. The atom labeling and molecular structures of **4** and **5** are shown in Figs. 1 and 3 respectively. Figs. 2 and 4 show the unit cell of complexes **4** and **5**.

Table 1. Experimental data for the X-ray diffraction studies.

	Complex (**4**)	Complex (**5**)
Empirical formula	$C_{26}H_{20}N_2S_3Sn$	$C_{29}H_{26}N_2S_3Sn$
Formula weight	575.31	617.39
Crystal system	monoclinic	triclinic
Space group	*P2₁/c*	*P-1*
a (Å)	9.696(2)	9.744(6)
b (Å)	14.773(3)	16.338(10)
c (Å)	17.466(4)	17.957(12)
α (°)	90	90.000(12)
β (°)	92.559(3)	100.735(11)
γ (°)	90	90.000(12)
V (Å^3)	2499.2(9)	2809(3)
Z	4	4
μ (mm^{-1})	1.289	1.153
D_c (g cm^{-3})	1.529	1.460
F(000)	1152	1248
Min, min/θ°	1.81 to 25.02	1.7 to 22.13
Limiting indices	–9<=h<=11, –17<=k<=16, –20<=l<=15,	–10<=h<=10, –14<=k<=17, –19<=l<=17,
Total reflection	12808	11405
Independent reflections	4393 (R_{int} = 0.0341)	6907 (R_{int} = 0.0894)
Max. and min. transmission	0.8819 and 0.6983	0.8934 and 0.8461
data/restraints/parameters	4393/0/369	6907/0/631
R_1 (all data)	0.0313	0.1590
wR_2 (all data)	0.0535	0.1252
R_1 (Final)	0.0545	0.0519
wR_2 (all data)	0.0594	0.0947
Goodness-of-fit on F^2	0.927	0.787
Residual electron density (e. Å^{-3})	0.388 and –0.495	0.411 and –0.365

The four primary bonds to tin in complex **4** are to the three benzyl groups and to the sulfur atom of the ligand, Sn(1)–C(15) 2.122(3), Sn(1)–C(21) 2.126(4), Sn(1)–C(9) 2.131(3) and Sn(1)–S(2) 2.4765(11) Å. In addition, there is also weak intramolecular Sn–N interaction (2.987(3) Å), thus providing a four-membered chelate ring with a bite angle, N–Sn-S, of 57.46°. The Sn–S bond length is a little longer than the sum of the covalent radii (2.42 Å) [18], which may be due to the bidentate functions of the HMBT. To perform valence extension, it requires the nitrogen atoms to be

close enough to tin atom. But the S and N donor atoms belong to the same moiety, so their positions are fixed and the deformation S–Sn–N angles cannot be very great. So the Sn–S bonds stretch a little to meet the coordinated requirement of N atom. The Sn–N distance lies between the sums of the covalent radii and van der Waals of Sn and N, 2.15 and 3.74 Å [5]. It is totally in agreement with the valence extension of the metal atom [19,20].

Table 2. Selected bond lengths (Å) and angles (°) of complex (**4**) and (**5**).

Complex **4**			
Sn(1)–C(15)	2.122(3)	Sn(1)–S(2)	2.4765(11)
Sn(1)–C(21)	2.126(4)	Sn(1)–N(1)	2.987(3)
Sn(1)–C(9)	2.131(3)		
C(15)–Sn(1)–C(21)	118.98(15)	C(9)–Sn(1)–S(2)	99.96(10)
C(15)–Sn(1)–C(9)	109.97(13)	C(9)–Sn(1)–N(1)	156.95(5)
C(21)–Sn(1)–C(9)	109.30(13)	C(15)–Sn(1)–N(1)	83.47(3)
C(15)–Sn(1)–S(2)	106.96(9)	C(21)–Sn(1)–N(1)	77.82(3)
C(21)–Sn(1)–S(2)	109.96(10)	S(2)–Sn(1)–N(1)	57.46(9)
Complex **5**			
Sn(1)–C(16)	2.145(13)	Sn(2)–C(52)	2.142(13)
Sn(1)–C(23)	2.162(11)	Sn(2)–C(45)	2.173(12)
Sn(1)–C(9)	2.164(12)	Sn(2)–C(38)	2.178(11)
Sn(1)–S(2)	2.454(4)	Sn(2)–S(5)	2.454(4)
Sn(1)–N(1)	3.117(11)	Sn(2)–N(2)	3.007(12)
C(16)–Sn(1)–C(23)	113.6(5)	C(45)–Sn(2)–C(38)	111.9(5)
C(16)–Sn(1)–C(9)	113.6(5)	C(52)–Sn(2)–S(5)	99.2(3)
C(23)–Sn(1)–C(9)	111.7(5)	C(45)–Sn(2)–S(5)	108.0(3)
C(16)–Sn(1)–S(2)	98.8(3)	C(38)–Sn(2)–S(5)	109.5(3)
C(23)–Sn(1)–S(2)	109.8(3)	S(2)–Sn(1)–N(1)	56.13(5)
C(9)–Sn(1)–S(2)	108.5(4)	C(9)–Sn(1)–N(1)	81.40(5)
C(52)–Sn(2)–C(45)	113.3(5)	C(16)–Sn(1)–N(1)	154.66(3)
C(52)–Sn(2)–C(38)	113.9(5)	C(23)–Sn(1)–N(1)	76.18(3)

Including the tin-nitrogen interaction, the geometry at tin becomes *cis*-trigonal bipyramidal. C(15), C(21), S(2) occupy the equatorial plane, whereas C(9) and N(1) are in axial positions with a C(9)–Sn-N(1) angle of 156.95°. The axial–Sn–axial angle is some distorted from the ideal octahedron angle of 180°, which is affected by the four-membered chelate rings mentioned above.

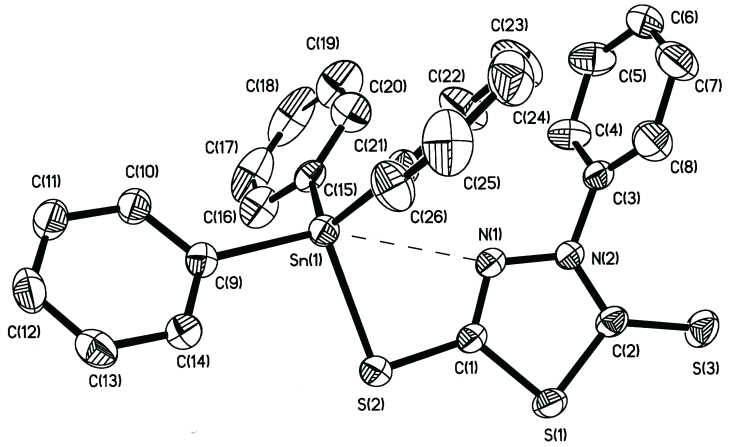

Figure 1. Molecular structure of complex (**4**). Probability ellipsoids drawn at 30%.

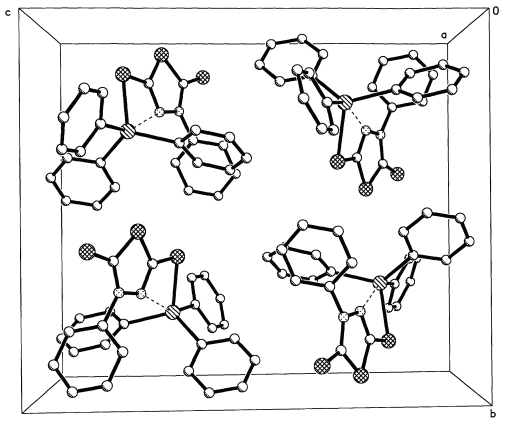

Figure 2. Cell unit of complex (**4**). Perspective view: (100).

In complex (**5**), the asymmetric unit contains two monomers (see Fig. 3), which are different from a crystallographic point of view. Conformations of the two independent molecules are almost the same, only with little differences in bond lengths and bond angles (see Table 2). Each monomer has a distorted *cis*-trigonal-bipyramidal geometry. For **5**, the environment of tin atom is similar to that of complex (**4**). Three C atoms and one S atom bond to tin primarily, and the N atom coordinated to tin through interaction. The Sn–C bond lengths are 2.145(13) Å, 2.162(11) Å, 2.164(12) Å, Sn–S 2.454(4) Å and Sn–N 3.117(11) Å respectively, which are all close to those of complex (**4**). The axial angle C(16)–Sn(1)–N(1) is 154.66(3)° with a chelate bite angle N–Sn–S of 56.13°.

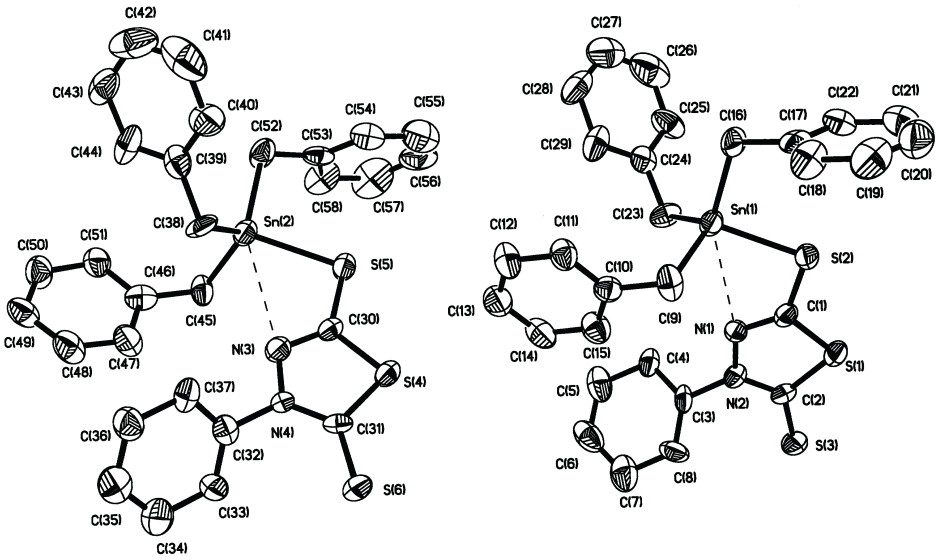

Figure 3. Molecular structure of complex (**5**). Probability ellipsoids drawn at 30%.

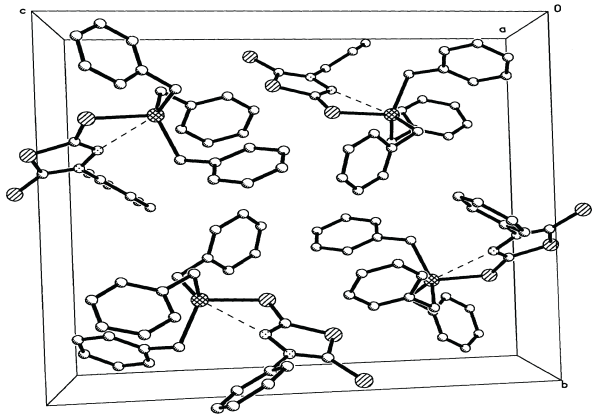

Figure 4. Cell unit of complex (**5**). Perspective view: (100).

The structural examination and the results of antitumor activity test of Sn(IV) complexes containing an N-donor atom revealed that, in the active tin complexes, the average Sn–N bond lengths are >2.39 Å. But the complexes where Sn–N bonds < 2.39 Å are inactive [5]. Such facts implied that predissociation of the ligand may be an important step in the mode of action of these complexes, while the coordinated ligand may favour transport of the active species to the site of action in the cells, where they are released by hydrolysis. From Table 2, we see that the Sn–N bonds of **4** and **5** are all longer than 2.39 Å, which is consistent with the results of bioactivity measurements, and evidenced the correlation of Sn–N bond lengths and antitumor activity.

Supplementary data: Atomic coordinates, thermal parameters and bond lengths and angles for complexes **4** and **5** have been deposited at the Cambridge Crystallographic Data Center, CCDC no. 183605 and 183601. Copies of this information may be obtained free of charge from the Director, CCDC, 2 Union Road, Cambridge CB2 1EZ, UK on request (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www. http://www. ccdc.cam.ac.uk).

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