

Note

Syntheses, characterizations and crystal structures of triorganotin(IV) derivatives with 2-mercapto-4-quinazolinone

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Abstract

The triorganotin(IV) derivatives of 2-mercapto-4-quinazolinone (HSqualone) of the type, R_3SnL ($R = Ph$ **1**, CH_3 **2**, $PhCH_2$ **3**, p -F- $PhCH_2$ **4**, o -F- $PhCH_2$ **5**, n -Bu **6**), were obtained by the reaction of the R_3SnCl and HSqualone with 1:1 molar ratio in benzene. All complexes **1–6** were characterized by elemental analyses, IR, 1H and ^{13}C NMR spectroscopy and the crystal structures of complexes **1–3** were also confirmed by X-ray crystallography. The structure analyses reveal that the tin atoms of complexes **1–3** are all distorted tetrahedral geometries. Furthermore, the dimeric structures in complexes **1–3** have also been found linked by intermolecular O–H···N or N–H···O hydrogen bonding interaction. Interestingly, the dimers of complexes **2** and **3** are further linked into one-dimensional chain through intermolecular C–H···S and C–H···O weak hydrogen bonding interactions, respectively.

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Keywords: 2-Mercapto-4-quinazolinone; Triorganotin(IV) complexes; Crystal structure

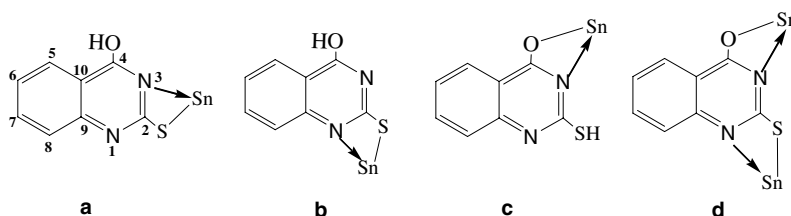
1. Introduction

Organotin(IV) complexes have been causing more and more attention for their industrial applications and potential biological activities [1–4]. Especially many varieties of organotin(IV) complexes have been synthesized and studied in the context of their antitumor potential [5,6]. It has been proved that 2-mercapto-4-quinazolinone (HSqualone) derivatives are one kind of the most potent PARP (poly(ADP-ribose) polymerase) inhibitors evaluated recently to avoid the lack of ATP and NAD causing mitochondrial dysfunction and cell damage [7–9]. These derivatives were also reported to have antifungal activity and antihypertensive effect [10,11]. Thus, the ligand HSqualone may act as valuable substrate to synthesize antitumor-active organotin compounds, it is also an important method to improve the antitumor activity [12–17].

Besides the consideration mentioned above, as a part of our studies on the coordination of organotin(IV) moieties with thiol sulfur and heterocyclic nitrogen [3,5,18], we choose the unsymmetrical ligand 2-mercapto-4-quinazolinone (HSqualone) which shows potential multidentate coordinate possibilities owing to the existence of a deprotonated thiol and more than one coordinative active heterocyclic nitrogen atom along with a hydroxyl oxygen atom, there exist four coordination modes (Scheme 1). To learn the nature of its versatile coordination chemistry, we have defined the reaction in 1:1 molar ratio (R_3SnCl :HSqualone), and obtained six triorganotin(IV) derivatives.

All complexes **1–6** were characterized by elemental analyses, IR, 1H and ^{13}C NMR. The structures of complexes **1–3** were determined by X-ray crystallographically. From the crystal structures of complexes **1–3**, we can see that the ligand adopts mode **b** to bond to tin atom through the 1-nitrogen and 2-sulfur donors, and complex **1** shows a dimer via O–H···N hydrogen bond, the supramolecular structure of complexes **2** shows a 1D infinite chain due to the existence of intermolecular O–H···N, C–H···S weak hydrogen

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Scheme 1.

bonds, the supramolecular structure of complexes **3** becomes a 1D chain through the N–H···O and C–H···O hydrogen bonds.

2. Results and discussion

2.1. Syntheses of the complexes 1–6

The synthesis procedure was as in Scheme 2:

We have obtained six new complexes from the reaction through the triorganotin(IV) chlorides and ligand 2-mercapto-4-quinazolinone, and obtained the single-tin triorganotin(IV) derivatives with single ligand coordinated. The oxygen atom from the hydroxyl has not participated in the coordination. We consider it was due to the reason that the coordinated capability of oxygen atom from hydroxyl is much weaker than sulfur atom in these reactions.

2.2. Spectra

The IR spectra show that the strong absorption at 2600 cm^{-1} in free ligand HSqualone due to the –SH group is absent in spectra of all complexes **1–6**. While in the far infrared spectra, the strong absorption which appears at the range of $310\text{--}295\text{ cm}^{-1}$ in the respective spectra of the complexes **1–6** and which is absent in the spectrum of the ligand, is assigned to the Sn–S stretching mode of vibration [19]. The absorption at 3440 cm^{-1} assigned to the O–H stretching mode of vibration in free ligand HSqualone is also observed in complexes **1–6**, which indicate that the hydroxyl group has not participated in the coordination. The $\nu(\text{C}=\text{N})$ band observed at $1562\text{--}1545\text{ cm}^{-1}$ in the spectra of all complexes **1–6**, is considerably shifted towards lower frequencies related to that of the free ligand owing to the displacement of electron density from N to Sn atom. It confirmed the coordination of the heterocyclic N to the tin atom and resulted in the weakening of the C=N bond

as reported in the literature [20]. The bands in the region $485\text{--}446\text{ cm}^{-1}$ are assigned to Sn–N stretching vibration. Besides, in organotin(IV) complexes, the IR spectra can provide useful information concerning the geometry of the SnC_n moiety [21]. In the cases of complexes **1–6**, the bands at 560 and 520 cm^{-1} for **1**, at 547 and 517 cm^{-1} for **2**, at 620 and 549 cm^{-1} for **3**, at 618 and 542 cm^{-1} for **4**, at 614 and 548 cm^{-1} for **5** and at 561 and 523 cm^{-1} for **6**, can be assigned to $\nu_{\text{as}}(\text{Sn–C})$ and $\nu_{\text{s}}(\text{Sn–C})$, respectively, suggesting non-planar SnC_3 fragments for triorganotin derivatives **1–6**.

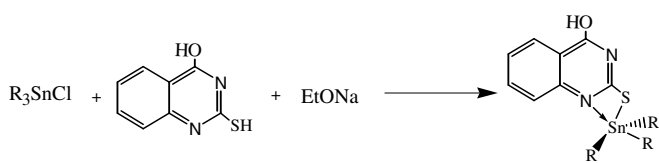
^1H NMR data show that the signal of the –SH proton (1.63 ppm) in the spectrum of the ligand is absent in all the complexes **1–6**, indicating the removal of the –SH proton. Furthermore, the hydroxyl group signal has chemical shift at the region of 3.85–4.75 ppm, indicating that the hydroxyl group involves no interaction with the center tin atom. The informations agree with what the IR data have revealed. The ^{13}C NMR spectra of all complexes **1–6** show a significant downfield shift of all carbon resonances. The shift is a consequence of an electron density transfer from the ligand to the acceptor.

2.3. Crystal structures of complexes 1–3

The crystal structures and supramolecular structures of complexes **1–3** are shown in Figs. 1(a,b), 2(a,b) and 3(a,b), respectively. All H atoms have been omitted for the purpose of clarity. Table 1 lists the crystal data and structure refinement parameters for complexes **1–3** and their selected bond lengths and angles are shown in Tables 2–4, respectively. Generally saying, each of the complexes **1–3** has a tetra-coordinated tin atom (Scheme 2) and the ligand HSqualone coordinate to center Sn atom by the coordination mode **b**. The detail analyses are as follows.

2.3.1. Structures of complex 1

The tin atom in complex **1** is tetra-coordinated and the ligand HSqualone acting as a bidentate S,N ligand adopts mode **b** to coordinate to tin atom and the bonding is through the deprotonated SH rather than the OH group. As shown in Fig. 1(a), the central tin atom of complex **1** forms four primary bonds: three to the phenyl groups and one to the sulfur atom. The corresponding C–Sn–C bond angles ranging from $106.8(4)^\circ$ to $115.9(4)^\circ$ are close to the theoretical tetrahedral angle but the C–Sn–S bond



(R=Ph **1**, R=Me **2**, R=PhCH₂ **3**, *p*-F-PhCH₂ **4**, *o*-F-PhCH₂ **5**, *n*-Bu **6**)

Scheme 2.

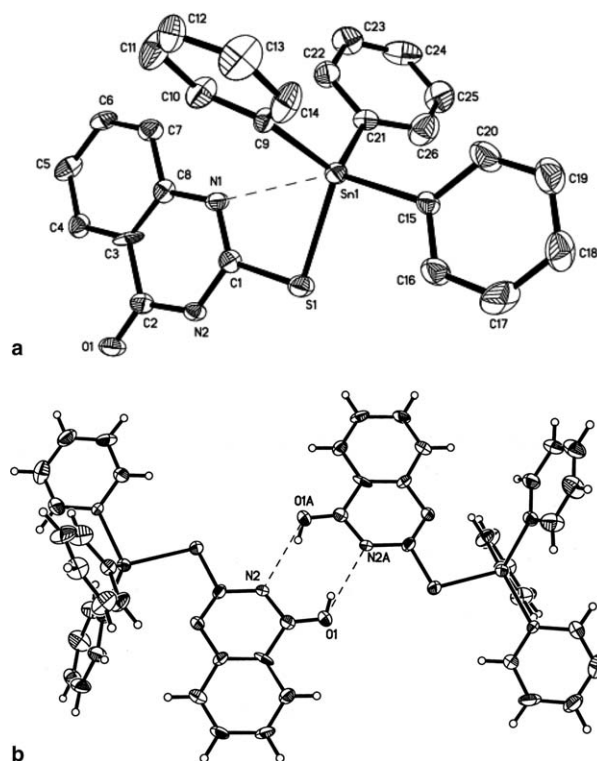


Fig. 1. (a) Molecular structure of complex **1**. (b) Dimeric structure of the complex **1**.

angles more acute and obtuse than it, largest deviations occurring in C15–Sn–S1 $96.8(3)^\circ$. This may attribute that there is an intramolecular Sn–N weak interaction between Sn1 and N1 atoms. The Sn1–N1 bond length ($3.048(9) \text{ \AA}$) is midway between the sums of the van der Waals and covalent

radii of tin and nitrogen ($2.15, 3.74 \text{ \AA}$) [22], which is longer than that of complex $\text{Ph}_3\text{Sn}(\text{Spym})$ (2.878 \AA) [5] but shorter than that reported in complex $\text{Ph}_3\text{Sn}(\text{MBZ})$ (3.07 \AA) and $\text{Ph}_3\text{Sn}(\text{MNBT})$ (3.14 \AA) [23,24]. The Sn1–S1 bond length ($2.450(3) \text{ \AA}$) is within the range reported for organotin(IV) complexes ($2.41\text{--}2.48 \text{ \AA}$) [25–27] and is similar to that reported for the complex $\text{Ph}_3\text{Sn}(\text{MNBT})$ (2.453 \AA) [24] and shorter than that of the complex $\text{Ph}_3\text{Sn}(\text{MTS})$ (2.47 \AA) [28].

It is worth noting that there exists intermolecular O–H \cdots N hydrogen bonding between nitrogen (N2) and hydroxyl oxygen (O \cdots N = 2.850 \AA), and these hydrogen bonding associates the adjacent two discrete molecules into a dimer structure in the solid (Fig. 1(b)).

2.3.2. Structures of complex 2

Similar to complex **1**, the structure of complex **2** is also tetra-coordinated and the ligand adopts the same coordinated mode **b**. The geometry at Sn in complex **2** is also a distorted tetrahedral with the C–Sn–C angles ranging from $106.0(3)^\circ$ to $115.7(3)^\circ$ and C–Sn–S angles ranging from $100.1(3)^\circ$ to $111.0(2)^\circ$, which is similar to that found in complex **1**. The bond length of Sn1–S1 ($2.4552(17) \text{ \AA}$) approaches to the sum of the covalent radii of tin and sulfur (2.42 \AA) [29] and is shorter than that of complex $\text{Me}_3\text{Sn}(\text{Spym})$ (2.463 \AA) [5]. While the bond distance of Sn1–N1 ($3.043(5) \text{ \AA}$) is slightly shorter than that the corresponding distance in complex **1** (3.048 \AA) but longer than that of complex $\text{Me}_3\text{Sn}(\text{Spym})$ (2.965 \AA) [5]. The C–S bond distance (C1–S1 $1.740(6) \text{ \AA}$) lies between the average value for the double C=S bond in thioureas (1.681 \AA) and the single C–S bond in the C–S–Me fragment (1.789 \AA) [30], so that it can be regarded

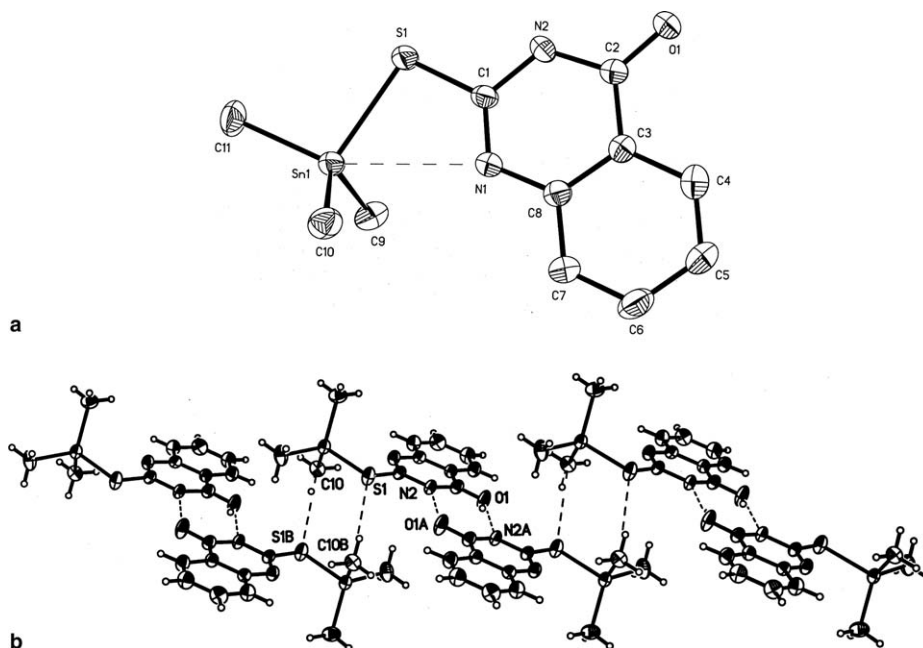


Fig. 2. (a) Molecular structure of complex **2**. (b) 1D Chain connected by intermolecular O–H \cdots N and C–H \cdots S hydrogen bonding.

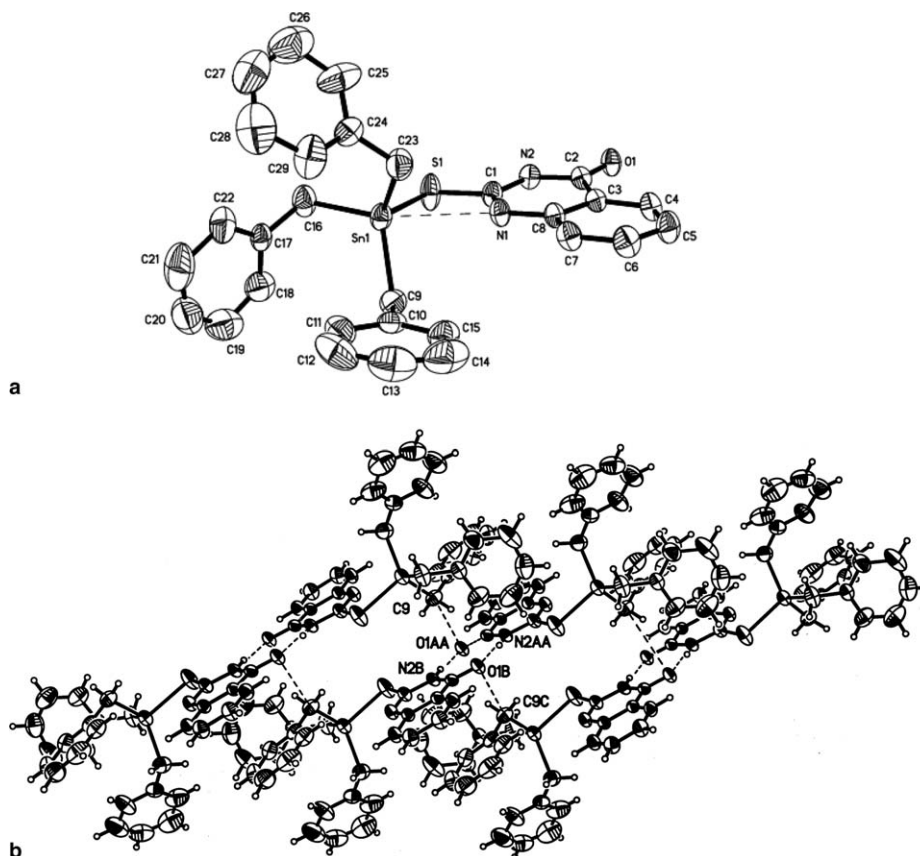


Fig. 3. (a) Molecular structure of complex **3**. (b) 1D chain connected by intermolecular N–H···O and C–H···O hydrogen bonding.

as C–S single bond and also suggesting that it has some double-bond character.

Hydrogen bonded dimeric units also exist in complex of **2** and that are further linked by auxiliary hydrogen bonding (C–H···S, C–S = 3.700 Å) to produce the chain structure (Fig. 2(b)).

2.3.3. Structures of complex **3**

The structure and coordinated mode of complex **3** is similar to complexes **1** and **2**. The geometry of tin atom is also distorted tetrahedral with C–Sn–C angles ranging from 111.9(3)° to 113.5(3)° and C–Sn–S angles ranging from 96.45(19)° to 112.4(2)°. Concerning the Sn–N bond, the bond length (Sn1–N1 2.954(4) Å) is longer than that in complex (PhCH₂)₃Sn(Spym) (2.724 Å) [5], while shorter than that in complexes **1** and **2** (3.043(5) and 3.048(9) Å). The Sn1–S1 bond length (2.4635(17) Å) is almost completely same with the length in complex (PhCH₂)₃Sn(Spym) (2.46 Å) [5] and shorter than that in complex (PhCH₂)₃Sn(MNBT) (2.49 Å) [31]. The C–S bond distance (C1–S1 1.752(6) Å) is similar to the C–S bond in complex **2**, also suggesting that the single C–S bond has some double-bond character.

Hydrogen bonded dimeric units also exist in the structure of **2** and that are further linked by auxiliary hydrogen bonding (C–H···O, C–O = 3.492 Å) produce the chain structure (Fig. 3(b)).

3. Conclusion

A series of triorganotin(IV) complexes based on 2-mercapto-4-quinazolinone have been synthesized and characterized. Detailed studies on the structures and spectra of these complexes indicate that there exist such an inclination the –SH group in 2-mercapto-4-quinazolinone is easily reacted with triorganotin(IV) moiety than the –OH group, so all the complexes are bonded with deprotonated –SH group with mononuclear structure. The geometry of the tin atom in each complex is tetra-coordinated and displays a distorted tetrahedral geometry. Besides, an intramolecular Sn–N weak interaction has also been found between central tin atom and N1 atom in the ligand. Interestingly, the uncoordinated –OH group and the N3 atoms in the ligand involves intermolecular O–H···N hydrogen bonding, which makes these complexes exist as dimers. Furthermore, 1D linear chains have been found in complexes **2** and **3** that are linked by the auxiliary intermolecular C–H···S (for complex **2**) or C–H···O (for complex **3**) weak hydrogen bonding.

4. Experimental details

4.1. Materials and measurements

Triphenyltin chloride, tri-*n*-butyltin chloride, trimethyl chloride and 2-mercapto-4-quinazolinone were commercially

Table 1
Crystal data collection and structure refinement parameters of complexes 1–3

Complexes	1	2	3
Empirical formula	C ₂₆ H ₂₀ N ₂ OSSn	C ₁₁ H ₁₄ N ₂ OSSn	C ₂₉ H ₂₆ N ₂ OSSn
Formula weight	503.17	340.99	569.27
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.515(9)	7.420(2)	8.431(3)
<i>b</i> (Å)	10.925(10)	9.817(4)	10.275(4)
<i>c</i> (Å)	12.000(11)	10.236(3)	30.292(11)
β (°)	102.953(11)	109.684(4)	93.778(6)
<i>V</i> (Å ³)	1141.4(18)	666.5(4)	2618.5(17)
<i>Z</i>	2	2	4
<i>D</i> _{calc} (Mg m ⁻³)	1.464	1.699	1.444
<i>F</i> (000)	504	336	1152
μ (mm ⁻¹)	1.227	2.055	1.079
Crystal size (mm)	0.43 × 0.37 × 0.29	0.45 × 0.29 × 0.21	0.47 × 0.41 × 0.24
θ Range	2.34–25.02°	2.18–25.02°	2.09–25.05°
Index ranges	–11 ≤ <i>h</i> ≤ 11, –5 ≤ <i>k</i> ≤ 12, –14 ≤ <i>l</i> ≤ 14	–7 ≤ <i>h</i> ≤ 8, –11 ≤ <i>k</i> ≤ 11, –11 ≤ <i>l</i> ≤ 12	–10 ≤ <i>h</i> ≤ 8, –10 ≤ <i>k</i> ≤ 12, –36 ≤ <i>l</i> ≤ 29
Reflections collected	4679	3355	13032
Unique reflections [<i>R</i> _{int}]	3326 [0.0431]	2263 [0.0258]	4571 [0.0292]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Maximum/minimum transmission	0.7174, 0.6205	0.6721, 0.4582	0.7818, 0.6310
Data, restraints, parameters	3326, 0, 280	2263, 0, 145	4571, 48, 307
GOF	1.024	1.032	1.006
Final <i>R</i> indices	<i>R</i> ₁ = 0.0735,	<i>R</i> ₁ = 0.0495,	<i>R</i> ₁ = 0.0509,
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.1730	<i>wR</i> ₂ = 0.1274	<i>wR</i> ₂ = 0.1184
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0977,	<i>R</i> ₁ = 0.0549	<i>R</i> ₁ = 0.0712,
	<i>wR</i> ₂ = 0.1872,	<i>wR</i> ₂ = 0.1313,	<i>wR</i> ₂ = 0.1291
Largest difference peak, hole (e Å ⁻³)	1.419, –0.677	2.901, –0.392	0.644, –0.643

Table 3
Selected bond lengths and angles for the complex 2

Bond	Distance (Å)	Bond	Distance (Å)
Sn1–C10	2.106(7)	Sn1–C9	2.108(7)
Sn1–C11	2.133(7)	Sn1–S1	2.4552(17)
Sn1–N1	3.043(5)	N1–C1	1.277(8)
S1–C1	1.740(6)		
Angle	Amplitude (°)	Angle	Amplitude (°)
C11–Sn1–S1	100.1(3)	C10–Sn1–C9	115.7(3)
C10–Sn1–S1	111.0(2)	C11–Sn1–C9	111.5(4)
C9–Sn1–S1	106.0(3)	C11–Sn1–C10	111.3(3)

Table 2
Selected bond lengths and angles for the complex 1

Bond	Distance (Å)	Bond	Distance (Å)
Sn1–C21	2.123(10)	Sn1–C9	2.125(9)
Sn1–C15	2.141(10)	Sn1–S1	2.450(3)
Sn1–N1	3.048(9)	N1–C1	1.293(13)
S1–C1	1.741(10)		
Angle	Amplitude (°)	Angle	Amplitude (°)
C15–Sn1–S1	96.8(3)	C21–Sn1–C9	115.9(4)
C21–Sn1–S1	111.53(3)	C15–Sn1–C9	106.8(4)
C9–Sn1–S1	114.1(3)	C21–Sn1–C15	109.8(4)

available and they were used without further purification. Tribenzyltin chloride, tri(*o*-fluorobenzyl)tin chloride and tri(*p*-fluorobenzyl)tin chloride were prepared by a standard method reported in the literature [32]. The melting points were obtained on a Kofler micro melting point apparatus

Table 4
Selected bond lengths and angles for the complex 3

Bond	Distance (Å)	Bond	Distance (Å)
Sn1–C23	2.144(7)	Sn1–C9	2.151(6)
Sn1–C16	2.160(6)	Sn1–S1	2.4635(17)
Sn1–N1	2.954(4)	N1–C1	1.293(7)
S1–C1	1.752(6)		
Angle	Amplitude (°)	Angle	Amplitude (°)
C9–Sn1–S1	108.9(2)	C16–Sn1–C9	111.9(3)
C16–Sn1–S1	96.45(19)	C23–Sn1–C9	113.5(3)
C23–Sn1–S1	112.4(2)	C23–Sn1–C16	112.4(3)

and are uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ¹H NMR and ¹³C NMR spectra were obtained on a Varian Mercury Plus 400 MHz NMR spectrometer operating at 400 and 100.6 MHz, respectively. Chemical shifts are given in ppm relative to Me₄Si in CDCl₃ solvent. Elemental analyses were performed with a PE-2400 II apparatus.

4.2. Syntheses of the complexes 1–6

4.2.1. [Ph₃Sn(Squalone)] (1)

Under dry nitrogen atmosphere the 2-mercapto-4-quinazolinone (0.178 g, 1 mmol) and sodium ethoxide (0.068 g, 1 mmol) were added in benzene (20 ml) in a Schlenk flask and stirred for about 10 min. Triphenyltin chloride (0.385 g, 1 mmol) was then added and stirring

continued for 12 h at 40 °C and then filtrated. The filtrate was gradually evaporated until a solid product was obtained. The solid was recrystallized from diethylether–petroleumether. Transparent colourless crystals of complex **1** were formed. Yield: 70%. M.p. 210–212 °C. Analysis: Found: C, 59.29; H, 3.91; N, 5.38. Calcd. for C₂₆H₂₀N₂OSSn: C, 59.23; H, 3.82; N, 5.31%. ¹H NMR (CDCl₃, δ ppm): 7.56–7.03 (m, 19H, aromatic-H), 4.31 (s, 1H, hydroxyl-H). ¹³C NMR (CDCl₃, δ ppm): 173.2 (C2), 166.71 (C4), 151.1 (C9), 131.0 (C10), 129.83 (C6, C7), 128.74 (C5, C8), 129.54 (*p*-C), 136.95 (*i*-C), 129.01 (*m*-C), 136.72 (*o*-C). IR (KBr, cm⁻¹): 303 ν(Sn–S); 447 ν(Sn–N); 560 ν_{as}(Sn–C); 520 ν_s(Sn–C); 1562ν (C=N); 3419ν (O–H).

4.2.2. [Me₃Sn(Squalone)] (2)

The procedure was the same as that of complex **1** and the crystalline complex **2** was obtained in diethylether. Yield: 76%. M.p. 90–92 °C. Analysis: Found: C, 38.65; H, 4.23; N, 8.16. Calcd. for C₁₁H₁₄N₂OSSn: C, 38.74; H, 4.14; N, 8.21%. ¹H NMR (CDCl₃, δ ppm): 7.68–7.26 (m, 4H, aromatic-H), 1.30–1.21 (m, 9H, CH₃), 3.85 (s, 1H, hydroxyl-H). ¹³C NMR (CDCl₃, δ ppm): 172.4 (C2), 166.8 (C4), 151.6 (C9), 130.2 (C10), 129.4 (C6, C7), 128.2 (C5, C8), –3.4 (CH₃). IR (KBr, cm⁻¹): 306 ν(Sn–S); 485 ν(Sn–N); 547 ν_{as}(Sn–C); 517 ν_s(Sn–C); 1550 ν(C=N); 3442 ν(O–H).

4.2.3. [(PhCH₂)₃Sn(Squalone)] (3)

The procedure was the same as that of complex **1** and the crystals of complex **3** was formed in diethylether. Yield: 82%. M.p. 205–207 °C. Analysis: Found: C, 61.25; H, 4.64; N, 5.01. Calcd. for C₂₉H₂₆N₂OSSn: C, 61.18; H, 4.60; N, 4.92%. ¹H NMR (CDCl₃, δ ppm): 7.38–6.84 (m, 19H, aromatic-H), 1.70–1.65 (m, 6H, PhCH₂), 4.71 (s, 1H, hydroxyl-H). ¹³C NMR (CDCl₃, δ ppm): 173.1 (C2), 166.2 (C4), 150.8 (C9), 130.6 (C10), 129.5 (C6, C7), 128.8 (C5, C8), 140.01 (*i*-C), 127.99 (*m*-C), 128.87 (*p*-C), 124.4 (*o*-C), 24.61 (CH₂-Ph). IR (KBr, cm⁻¹): 308 ν(Sn–S); 446 ν(Sn–N); 620 ν_{as}(Sn–C); 549 ν_s(Sn–C); 1545 ν(C=N); 3417 ν(O–H).

4.2.4. (*p*-F-PhCH₂)₃Sn(Squalone) (4)

The procedure was the same as that of complex **1**. Yield: 71%. M.p. 216–218 °C. Analysis: Found: C, 55.94; H, 3.80; N, 4.42. Calcd. for C₂₉H₂₃F₃N₂OSSn: C, 55.88; H, 3.72; N, 4.49%. ¹H NMR (CDCl₃, δ ppm): 7.32–6.89 (m, 16H, aromatic-H), 2.30–1.18 (m, 6H, *p*-F-PhCH₂), 4.73 (s, 1H, hydroxyl-H). ¹³C NMR (CDCl₃, δ ppm): 173.4 (C2), 165.6 (C4), 152.1 (C9), 133.2(C10), 129.7 (C6, C7), 129.5 (C5, C8), 160.6 (*p*-C), 135.7 (*i*-C), 128.9 (*m*-C), 128.42 (*o*-C), 23.2 (CH₂-Ph-F-*p*). IR (KBr, cm⁻¹): 310 ν(Sn–S); 455 ν(Sn–N); 618 ν_{as}(Sn–C); 542 ν_s(Sn–C); 1552 ν(C=N); 3415 ν(O–H).

4.2.5. (*o*-F-PhCH₂)₃Sn(Squalone) (5)

The procedure was the same as that of complex **1**. Yield: 76%. M.p. 220–222 °C. Analysis: Found: C, 55.91; H, 3.78; N, 4.39. Calcd. for C₂₉H₂₃F₃N₂OSSn: C, 55.88; H, 3.72; N,

4.49%. ¹H NMR (CDCl₃, δ ppm): 7.35–6.92 (m, 16H, aromatic-H), 2.26–1.20 (m, 6H, *o*-F-PhCH₂), 4.75 (s, 1H, hydroxyl-H). ¹³C NMR (CDCl₃, δ ppm): 174.6 (C2), 167.7 (C4), 153.8 (C9), 131.5 (C10), 128.65 (C6, C7), 129.77 (C5, C8), 132.3 (*p*-C), 128.1 (*i*-C), 128.7 (*m*-C), 160.1 (*o*-C), 24.4 (CH₂-Ph-F-*p*). IR (KBr, cm⁻¹): 304 ν(Sn–S); 450 ν(Sn–N); 614 ν_{as}(Sn–C); 548 ν_s(Sn–C); 1549 ν(C=N); 3414 ν(O–H).

4.2.6. *n*-Bu₃Sn(Sdmpym) (6)

The procedure was the same as that of complex **1**. Yield: 74%. M.p. 203–205 °C. Analysis: Found: C, 51.36; H, 6.98; N, 6.06. Calcd. for C₂₀H₃₂N₂OSSn: C, 51.41; H, 6.90; N, 6.00%. ¹H NMR (CDCl₃, δ ppm): 7.59–7.24 (m, 4H, aromatic-H), 1.79–1.14 (m, 27H, *n*-Bu), 3.92 (s, 1H, hydroxyl-H). ¹³C NMR (CDCl₃, δ ppm): 173.6 (C2), 166.7 (C4), 152.2 (C9), 131.6 (C10), 128.78 (C6, C7), 128.6 (C5, C8), 14.5, 24.5, 28.3, 31.4(*n*-Bu). IR (KBr, cm⁻¹): 296 ν(Sn–S); 472 ν(Sn–N); 561 ν_{as}(Sn–C); 523 ν_s(Sn–C); 1558 ν(C=N); 3420 ν(O–H).

4.3. X-ray structure analyses of **1–3**

All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer. Correction for semi-empirical from equivalents 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 Mo K α radiation ($\lambda = 0.71073$ Å) at 298 K. The positions of hydrogen atoms were calculated, and their contributions were included in structural factor calculations.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 263946, 263954, and 263949 for complexes **1–3**, respectively. Copies of these information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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References

- [1] C.L. Ma, J.H. Zhang, G.R. Tian, R.F. Zhang, J. Organomet. Chem. 690 (2005) 519.

- [2] S.K. Duboy, U. Roy, *Appl. Organomet. Chem.* 17 (2003) 3.
- [3] C.L. Ma, Y. Shi, R.F. Zhang, Q. Jiang, *Polyhedron* 24 (2005) 1109.
- [4] L.F. Tang, Z.H. Wang, W.L. Jia, Y.M. Xu, J.T. Wang, *Polyhedron* 19 (2000) 381.
- [5] C.L. Ma, Y. Shi, Q. Jiang, *Heteroatom. Chem.* 16 (2005) 69.
- [6] M. Gielen, *Appl. Organomet. Chem.* 16 (2002) 481.
- [7] G. Kulcsar, T. Kalai, E. Osz, C.P. Sar, J. Jeko, B. Sumegi, K. Hideg, *ARKIVOC (Part V)* (2003).
- [8] J. Griffin, S. Srinivasan, K. Bowman, H.A. Kalvert, N.J. Curtin, D.R. Newel, L.C. Pemberton, B.T. Olding, *J. Med. Chem.* 41 (1998) 5247.
- [9] L. Tentori, C. Leonetti, M. Scarsella, G. d'Amati, I. Portarena, G. Zupi, E. Bonmassar, G. Graziani, *Blood* 99 (2002) 2241.
- [10] K.M. Shakhadoyatov, S. Yangibaev, L.M. Yun, C.S. Kadirov, *Chem. Natl. Comp.* 18 (1982) 106.
- [11] K.C. Liu, L.Y. Hsu, *Arch. Pharm.* 318 (1985) 502.
- [12] G.K. Sandhu, *J. Organomet. Chem.* 412 (1991) 31.
- [13] R. Barbieri, L. Pellerito, G. Ruisi, M.T. Lo Giudice, F. Huber, G. Atassi, *Inorg. Chim. Acta.* 66 (1982) 39.
- [14] F. Huber, G. Roge, L. Carl, G. Atassi, F. Spreafico, S. Filippeschi, R. Barbieri, A. Silvestri, E. Rivarola, G. Ruisi, F. Di Bianca, G. Alonzo, *J. Chem. Soc., Dalton Trans.* (1985) 523.
- [15] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* 16 (1985) 73.
- [16] M. Gielen, M. Vornefeld, H. Preut, *Appl. Organomet. Chem.* 6 (1992) 597.
- [17] M. Gielen, H. Ma, *Metal Based Drugs* 4 (1997) 193.
- [18] C.L. Ma, J.F. Sun, Y. Shi, *J. Organomet. Chem.* 690 (2005) 1560.
- [19] J.R. May, W.R. Mc Whinnie, R.C. Pollerm, *Spectrochim. Acta* 27A (1971) 969.
- [20] C. Pettinari, F. Marchetti, R. Pettinari, D. Martini, A. Drozdov, S. Troyanov, *Inorg. Chim. Acta* 325 (2001) 103, and references therein.
- [21] R.C. Poller, *The Chemistry of Organotin Compounds*, Logos Press, London, 1970, p. 221.
- [22] A. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [23] C.V. Rodarte de Moura, A.P.G. de Sousa, R.M. Silva, A. Abras, M. Hörner, A.J. Bortoluzzi, C.A.L. Filgueiras, J.L. Wardell, *Polyhedron* 18 (1999) 2961.
- [24] C.L. Ma, Q. Jiang, R.F. Zhang, *Polyhedron* 23 (2003) 4169.
- [25] D.N. Rau, Ph.D. Thesis, University of Massachusetts, USA, 1988, University Microfilm International, Ann Arbor, MI, 1990.
- [26] O. Jimenez-Sandoval, R. Cea-Olivares, S. Hernandez-Ortega, *Polyhedron* 16 (1997) 4129.
- [27] S.W. Ng, C. Wei, K.V.G. Das, T.C.W. Mak, *J. Organomet. Chem.* 334 (1987) 283.
- [28] L. Petrilli, F. Caruso, E. Rivarola, *Main Group Met. Chem.* 17 (1994) 439.
- [29] J.E. Huheey, *Inorganic Chemistry*, third ed., Harper Int., Cambridge, 1983.
- [30] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. II* (1987) S1.
- [31] C.L. Ma, Q. Jiang, R.F. Zhang, *Polyhedron* 23 (2004) 779.
- [32] K. Sisido, Y. Takeda, Z. Kinugawa, *J. Am. Chem. Soc.* 83 (1961) 538.