Syntheses and Crystal Structure of Six-coordinated Diorgnotin Complexes with 2,5-Dimercapto-4-phenyl-1,3,4-thiodiazole†

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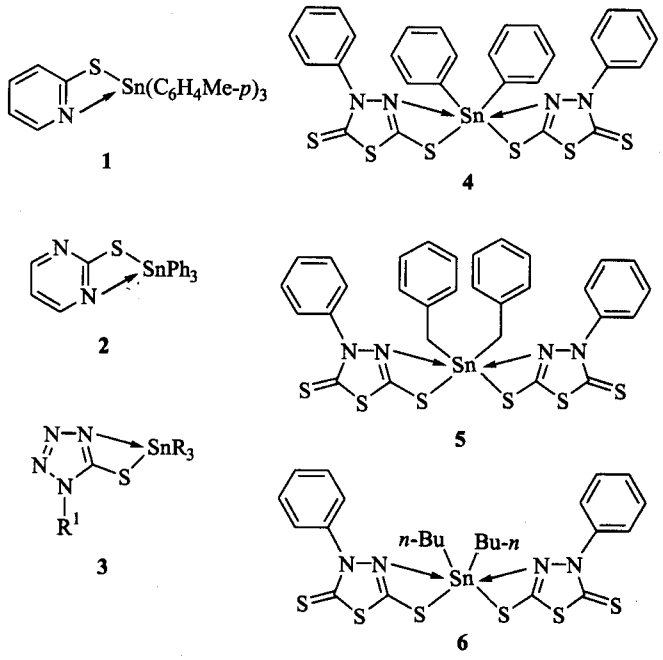
The reactions of diorganotin dichloride [Ph_2SnCl_2, $(PhCH_2)_2SnCl_2$ or $(n\text{-}Bu)_2SnCl_2$] with potassium salt of 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole gave complexes $R_2Sn(S_3N_2C_8H_5)_2$ (4: R = Ph; 5: R = $PhCH_2$ and 6: R = *n*-Bu), respectively. Characterizations were carried out for all complexes by IR, ^1H NMR spectra and X-ray crystallography analysis. Including the Sn···N interaction, the three complexes all have six-coordinated distorted octahedral geometry. Based on the requence of stereochemical constraint sequence, phenyl ≈ benzyl > *n*-butyl, the less the effect of the stereochemical constraint of R groups, the shorter the Sn···N length. In complexes 5 and 6, there exist S···S weak intra-molecular interactions, through which the complexes are dissociated into loose 2D polymers. All three complexes show antitumour activity in bioactivity measurements.

Keywords 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole, X-ray crystallography, diorganotin, chelate

Introduction

Organotin complexes exhibiting antitumour properties against a wide panel of tumoral cell lines of human origin and coordination chemistry of tin is extensive with various geometries, and coordination numbers are known for both inorganic and organometallic complexes.[1] Recently, attention has been devoted to the study of weak interaction of tin and organotin species,[2-5] because the occurrence of inter- or intra-molecular interaction gives access to higher coordinated complexes. An important research area concerns complexes in which tin bonds to S, N donor ligands, such as intramolecular coordination in complexes **1** and **2**,[6,7] intermolecular coordination in triphenyl(4-pyridinethiolato)stannane,[8] and intra-/inter-molecular interactions in complex **3** (Scheme 1).[9] The crystal structures of triphenyltin 1-methyltetrazole-5-thiolate and triphenyltin benzoxazole-2-thiolate have been shown to contain five-coordinated units.[10] As a receptor, diorganotin complexes can receive more donor atoms than triorganotin, thus having the possibility of generating higher coordination numbers, and there are few studies on the coordination of diorganotin containing Sn···N weak interaction.[11] In this paper we carried out the reaction of three diorganotin complexes, Ph_2SnCl_2, $(PhCH_2)_2SnCl_2$ and $(n\text{-}Bu)_2SnCl_2$, with the potassium salt of 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole (bismothol) to obtain the complexes $R_2Sn(S_3N_2C_8H_5)_2$ (**4**: R = Ph; **5**: R = $PhCH_2$ and **6**: R = *n*-Bu). They were characterized by elemental analysis, IR, ^1H NMR spectroscopy and X-ray diffraction analysis, and the effect of different R groups on the coordination was investigated.

Scheme 1



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Experimental and structural determination

Physical measurements

The reactions were carried out under a nitrogen atmosphere using standard Schlenk and vacuum techniques. The benzene solvent was distilled under nitrogen from sodium immediately before use. Melting points were determined using a Kofler instrument and uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer, and samples were prepared as KBr discs. ^{1}H NMR spectra were obtained on a Jeo-FX-90Q NMR spectrometer, and chemical shifts were relative to Me_4Si in $CDCl_3$ solvent. Elemental analyses were performed with a PE-2400II apparatus.

Crystal structure determination

X-Ray crystallographic studies carried out on a Bruker Smart 1000 diffractometer fitted with graphite monochromator Mo Kα radiation. Corrections were applied for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program system. All non-H atoms were included in the model at their calculated positions.

In vitro antitumour activity tests

Samples for antitumour activity tests were prepared by dissolving complexes **4**, **5** and **6** in DMSO, diluting the solution with water to concentration 10 μg/mL, and then the inhibition rate against culture cells of Ekrlich ascites carcinoma was measured as described in the literature.[12]

Synthesis of bis-(2,5-dimercapto-4-phenyl-1,3,4-thiodiazolyl) diphenyltin (**4**)

A mixture of bismothol (0.53 g, 2 mmol) and Ph_2SnCl_2 (0.344 g, 1 mmol) in benzene (20 mL) in a Schlenk flask was stirred for 12 h at 50 ℃, 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. 145—147 ℃; ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 6.67—7.59 (m, $^3J_{Sn-H}$ = 84 Hz, 20H); 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}. Anal. calcd for $C_{28}H_{20}N_4S_6Sn$: C 46.48, H 2.79, N 7.74; found C 46.45, H 2.77, N 7.78.

Synthesis of bis-(2,5-dimercapto-4-phenyl-1,3,4-thiodiazolyl) dibenzyltin (**5**)

This was similarly prepared as **4** from bismothol (0.53 g, 2 mmol) and $(PhCH_2)_2SnCl_2$ (0.37 g, 1 mmol) in benzene (20 mL). Colourless crystals of complex **5** were recrystallized from dichloromethane-hexane. Yield 83%, m.p. 150—152 ℃; ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 6.67—7.59 (m, $^3J_{Sn-H}$ = 84 Hz, 20H), 2.68—3.26 (m, $^2J_{Sn-H}$ = 72 Hz, 4H); 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}. Anal. calcd for $C_{30}H_{24}N_4S_6Sn$: C 47.94, H 3.22, N 7.45; found C 47.92, H 3.25, N 7.44.

Synthesis of bis-(2,5-dimercapto-4-phenyl-1,3,4-thiodiazolyl) dibutyltin (**6**)

This was similarly prepared as **4** from bismothol (0.53 g, 2 mmol) and $(n\text{-}Bu)_2SnCl_2$ (0.30 g, 1 mmol) in benzene (20 mL). Colourless crystals of complex **6** were recrystallized from ether-dichloromethane. Yield 85%, m.p. 140—142 ℃; ^{1}H NMR ($CDCl_3$, 90 MHz) δ: 6.67—7.59 (m, 10H), 1.10—1.75 (m, $^2J_{Sn-H}$ = 70 Hz, 12H), 0.90—1.10 (t, $^3J_{Sn-H}$ = 64 Hz, 6H); 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 $C_{24}H_{28}N_4S_6Sn$: C 42.17, H 4.13, N 8.20; found C 42.15, H 4.15, N 8.17.

Results and discussion

Spectroscopic analysis

The IR absorption related to Sn—S appears at 441 cm^{-1} for **4**, 449 cm^{-1} for **5**, 445 cm^{-1} for **6**, where ν(Sn—S) modes have been detected for a number of organotin (IV)-sulfur derivatives.[13-15] In addition, ν_{as}(Sn—C) and ν_s(Sn—C) appear at 537, 495 cm^{-1} for **4**, 582, 492 cm^{-1} for **5** and 583, 493 cm^{-1} for **6**,[16] respectively, suggesting that the ligand coordinated in the thiol-form rather than the thione-form. In the ^{1}H NMR spectra of all three complexes, the aryl signal is at δ 6.67—7.59. The ^{1}H shift of methylene is at δ 2.68—3.26 in **5**, and the ^{1}H shigts of *n*-butyl occur at δ 1.10—1.75 and 0.90—1.10.

Biologic activity measurement

The antitumour activity tests *in vitro* showed that the inhibition rates (%) of **4**, **5** and **6** against culture cells of Ekrlich ascites carcinoma are 72, 77 and 83, respectively, so the complexes have higher antitumour activity to Ehrlich ascites carcinoma than *cis*-[$Pt(NH_3)_2Cl_2$] (**55**).

Crystal structures of **4**, **5** *and* **6**

The crystal data and refinement details are given in Table 1 and the selected bond distances and angels in Table 2. The atom labeling and molecular structures of **4**, **5** and **6** are shown in Figs. 1, 3 and 5, respectively. Figs. 2, 4 and 6 show the packing of complexes **4**, **5** and

Table 1 Crystal data and refinement details for complexes **4**, **5** and **6**

Data and details	Complex **4**	Complex **5**	Complex **6**
Empirical formula	$C_{28}H_{20}N_4S_6Sn$	$C_{30}H_{24}N_4S_6Sn$	$C_{24}H_{28}N_4S_6Sn$
Formula weight	723.53	751.58	683.55
Temperature (K)	293(2)	298(2)	298(2)
Wavelength (nm)	0.071073	0.071073	0.071073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2_1/c$	P-1	$P2_1/m$
Unit cell dimensions			
a (nm)	1.1991 (3)	1.0507 (5)	0.7236 (2)
b (nm)	2.2248 (5)	1.1603 (5)	2.3105 (6)
c (nm)	1.1412 (3)	1.3401 (6)	0.9370 (3)
α (°)	90	88.551(8)	90
β (°)	96.010 (3)	78.629(8)	108.236(4)
γ (°)	90	85.806(9)	90
Volume (nm^3)	3.028 (1)	1.597 (1)	1.488 (7)
Z	4	2	2
Density (calcd) (Mg/m^3)	1.587	1.563	1.526
Absorption coefficient (mm^{-1})	1.284	1.219	1.299
Max/min. transmission factors	0.6994 and 0.5662	0.9304 and 0.7925	0.6965 and 0.5094
F(000)	1448	748	672
Crystal size (mm^3)	0.50 × 0.40 × 0.30	0.20 × 0.10 × 0.06	0.60 × 0.50 × 0.30
θ Range for data collection (°)	1.94 to 25.02	2.26 to 23.32	2.89 to 25.03
Index ranges	$-13 \leqslant h \leqslant 14$ $-18 \leqslant k \leqslant 26$ $-12 \leqslant l \leqslant 13$	$-11 \leqslant h \leqslant 11$ $-10 \leqslant k \leqslant 12$ $-14 \leqslant l \leqslant 12$	$-8 \leqslant h \leqslant 5$ $-27 \leqslant k \leqslant 27$ $-11 \leqslant l \leqslant 10$
Reflections collected	7185	6613	7201
Independent reflections	2583	4518	2559
R(int)	0.0249	0.0967	0.0323
Refinement method	Full-matrix l.s. on F^2	Full-matrix l.s. on F^2	Full-matrix l.s. on F^2
Number of parameters	197	370	172
Goodness-of-fit on F^2	1.029	0.763	0.984
Final R indices [$I > 2.0\sigma(I)$]	$R_1 = 0.0455$, $wR_2 = 0.0958$	$R_1 = 0.0634$, $wR_2 = 0.1025$	$R_1 = 0.0414$, $wR_2 = 0.0975$
R indices (all data)	$R_1 = 0.0551$, $wR_2 = 0.1002$	$R_1 = 0.2203$, $wR_2 = 0.1436$	$R_1 = 0.0563$, $wR_2 = 0.1055$
Final weighting scheme	$w = 1/[S^2(F_o^2) + (0.0303P)^2 + 20.7943P]$, $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[S^2(F_o^2) + (0.0328P)^2 + 0.0000P]$, $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[S^2(F_o^2) + (0.0651P)^2 + 0.0000P]$, $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole ($e \cdot nm^{-3}$)	688 and −819	578 and −750	831 and −410

6, respectively.

Complex **4** shows that, in the unit cell, the tin atom is bound to two sulfur atoms of the bismothol. The Sn—S distance 0.2472 nm is consistent with the sum of the covalent radii 0.244 nm[17] and close to the length of the similar bonds triphenyl (5-mercapto-1-phenyl-1, 2, 3, 4-tetrazolato)tin 0.2482(1) nm[6] but shorter than the value of 0.2565 (4) nm in **3**.[5] In addition, there are weak intramolecular Sn···N interaction (0.299 and 0.2994 nm), thus providing two 4-membered chelate rings with a bite angle, N-Sn-S, of 57.60°. The Sn···N distance is midway between the sums of the van der Waals and covalent radii of Sn and N (0.375[18] and 0.215 nm), respectively.[19]

Including the tin-nitrogen interaction,[10] the geometry at Sn becomes distorted *trans*-octahedral. The two nitrogen atoms and two sulfur atoms of bismothol occupy the equatorial plane, whereas the carbon atoms of phenyl groups are in axial positions with a C(9)-Sn-C(9A) angle of 118.2°. The axial-Sn-axial angle is well distorted from the ideal octahedron angle which is strongly affected by two 4-mem-

Table 2 Selected bond lengths (nm) and angles (°) for complexes **4**, **5**, and **6**

Complex 4			
Sn(1)—N(1)	0.2994(4)	C(2)—S(1)	0.1747(5)
Sn(1)—N(1)	0.2994(4)	C(1)—S(2)	0.1737(5)
Sn(1)—S(2)	0.2472(1)	C(2)—S(3)	0.1660(5)
Sn(1)—C(9)	0.2118(5)	C(2)—N(2)	0.1357(6)
C(1)—N(1)	0.1286(6)	N(1)—N(2)	0.187(6)
C(1)—S(1)	0.1741(5)		
C(9)-Sn(1)-S(2)	113.7(1)	N(1)-Sn(1)-S(2)	57.60(9)
C(9)-Sn(1)-S(2A)	109.4(2)	N(1)-Sn(1)-S(2A)	146.46(9)
C(9)-Sn(1)-N(1)	85.21(2)	S(2)-Sn(1)-S(2A)	88.91(7)
C(9)-Sn(1)-N(1A)	82.49(2)	Sn(1)-S(2)-C(1)	94.6(2)
C(9)-Sn(1)-C(9A)	118.2(3)	S(2)-C(1)-N(1)	123.6(4)
Complex 5			
Sn(1)—N(1)	0.299(1)	C(1)—S(3)	0.1721(1)
Sn(1)—N(3)	0.3099(1)	C(2)—S(4)	0.1709(1)
Sn(1)—S(3)	0.2462(4)	C(2)—N(2)	0.1318(1)
Sn(1)—S(5)	0.2459(4)	N(1)—N(2)	0.1424(1)
Sn(1)—C(17)	0.2126(1)	S(3)···S(5)	0.3424
Sn(1)—C(24)	0.2106(1)	S(5)···S(5A)	0.3488
C(1)—N(1)	0.1274(1)	S(1)···S(1A)	0.3597
C(1)—S(1)	0.1741(1)	S(2)···S(3)	0.3619
C(2)—S(1)	0.1696(1)	S(2)···S(1)	0.3716
C(17)-Sn(1)-S(3)	102.3(4)	N(1)-Sn(1)-N(3)	155.9(4)
C(17-Sn(1)-S(5)	104.8(4)	N(1)-Sn(1)-S(3)	57.60(3)
C(17)-Sn(1)-N(1)	118.2(4)	N(1)-Sn(1)-S(5)	146.80(3)
C(17)-Sn(1)-N(3)	88.9(4)	N(3)-Sn(1)-S(3)	146.1(3)
C(17)-Sn(1)-C(24)	131.6(5)	N(3)-Sn(1)-S(5)	57.08(2)
C(24)-Sn(1)-S(3)	111.8(4)	S(3)-Sn(1)-S(5)	89.48(1)
C(24)-Sn(1)-S(5)	108.7(4)	Sn(1)-S(3)-C(1)	94.59(1)
C(24)-Sn(1)-N(1)	84.15(4)	S(3)-C(1)-N(1)	123.6(4)
C(24)-Sn(1)-N(3)	86.59(4)		
Complex 6			
Sn(1)—N(1)	0.2923(3)	C(2)—S(1)	0.1747(5)
Sn(1)—N(1A)	0.292(3)	C(1)—S(2)	0.1737(5)
Sn(1)—S(2)	0.2481(1)	C(2)—S(3)	0.1660(5)
Sn(1)—S(2A)	0.2481(1)	C(2)—N(2)	0.1357(6)
Sn(1)—C(9)	0.2150(7)	N(1)—N(2)	0.1387(6)
Sn(1)—C(13)	0.2136(8)	S(2)···S(1A)	0.3361
C(1)—N(1)	0.1286(6)	S(2)···S(2A)	0.3494
C(1)—S(1)	0.1741(5)		
C(9)-Sn(1)-S(2)	107.02(1)	N(1)-Sn(1)-S(2A)	147.90(7)
C(9)-Sn(1)-C(13)	129.2(3)	N(1A)-Sn(1)-S(2A)	58.50(7)
C(9)-Sn(1)-N(1)	82.54(8)	S(2)-Sn(1)-S(2A)	89.50(6)
C(13)-Sn(1)-S(2)	108.47(1)	Sn(1)-S(2)-C(1)	94.59(1)
C(13)-Sn(1)-N(1)	86.16(9)	S(2)-C(1)-N(1)	123.6(4)
N(1)-Sn(1)-S(2)	58.50(7)		

bered chelate rings mentioned above. This structure is different from that of the similar six-coordinated complex **3** with weak interaction,[5] in which the Sn atom was described as a capped trigonal bipyramid with the weakly interacting N atom in the capping position.

With intramolecular tin-nitrogen interaction, crystallines **5** and **6** have similar distorted octahedral geometry to **4**. For **5**, the Sn—C bond lengths are 0.2126 and

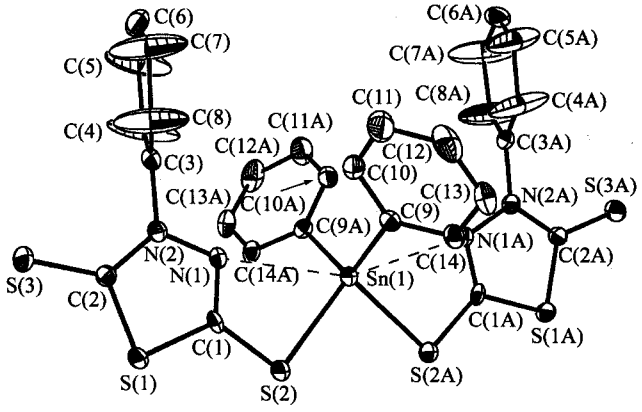

Fig. 1 Molecular structure of complex **4**.

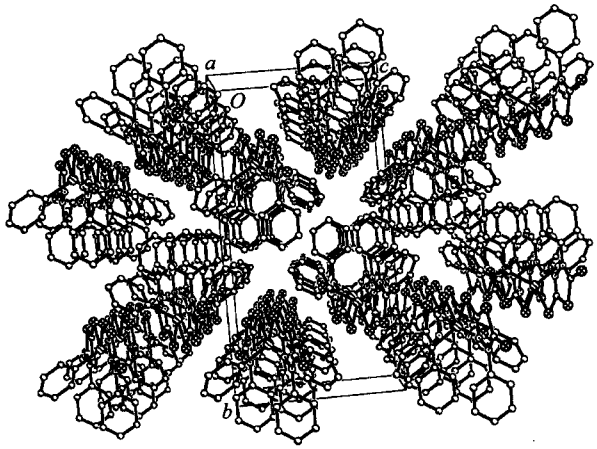

Fig. 2 Cell unit packing of complex **4**.

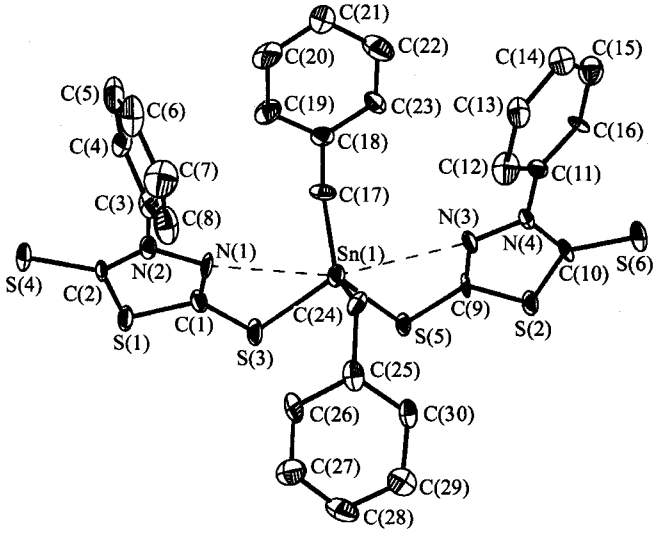

Fig. 3 Molecular structure of complex **5**.

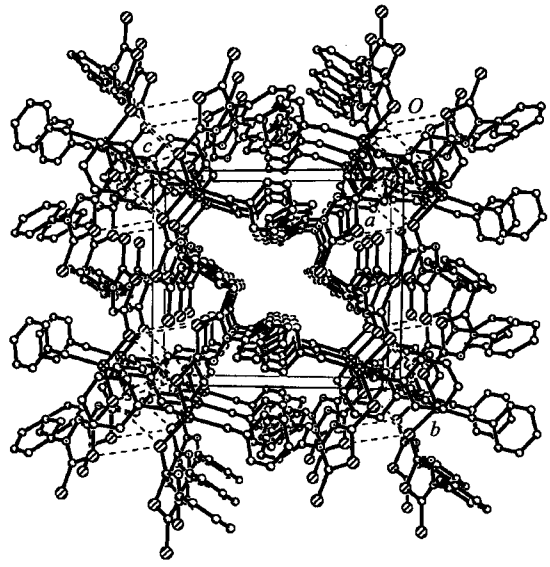

Fig. 4 Cell unit packing of complex **5**.

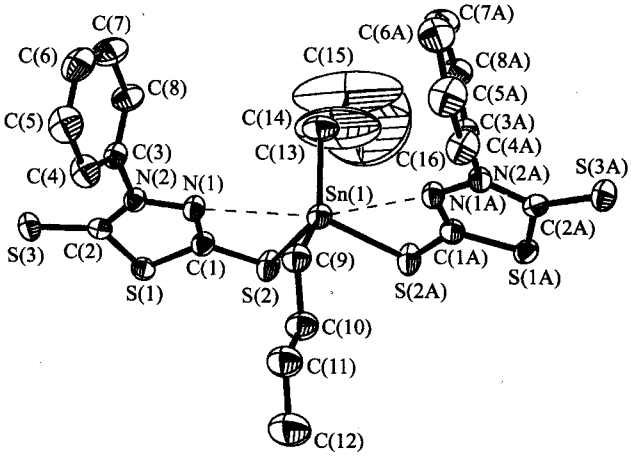

Fig. 5 Molecular structure of complex **6**.

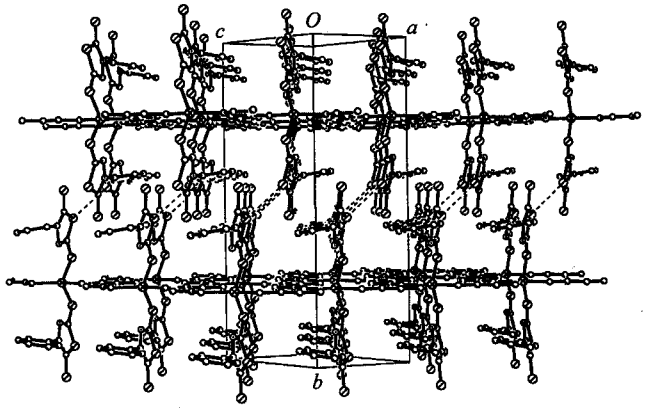

Fig. 6 Cell unit packing of complex **6**.

0.2106 nm; Sn—S 0.2462 and 0.2459 nm, Sn ··· N 0.299 and 0.3099 nm. The axial angle C(17)-Sn(1)-C(24) is 131.6(5)° with a chelate bite angle N-Sn-S of 57.41°. The Sn atom is displaced by 0.00509 nm from the geometric center of the equatorial plane of S(3), S(5), N(1) and N(3). For **6**, Sn—C bond lengths are 0.2150 and 0.2136 nm, Sn—S 2.481 and 0.2481 nm, Sn···N 0.292 and 0.2923 nm. The axial angle C(9)-Sn(1)-C(13) is 129.2(3)° with a chelate bite angle N-Sn-S of 58.50°. The Sn atom is displaced by 0.00827 nm from the geometric center of the equatorial plane of S(2), S(2A), N(1) and N(1A). From the data, we can see that com-

plexes **4** and **5** have similar Sn···N intra-molecular length, but the Sn···N length is a little shorter in **6**. Based on thestereo bulky constraint sequence, phenyl ≈ benzyl > *n*-butyl, it can be inferred that the less the effect of stereochmical constraints of R groups, the shorter the Sn···N length.

In complexes **5** and **6**, there exists S···S weak interaction called as intramolecular interaction,[20] through which the complexes are dissociated into loose 2D polymers. The intra- and inter-molecular non-bonded interactions seem to be attractive from the viewpoint of molecular recognition in chemical reactions[21] and medical biochemistry.[22] As shown in the cell unit packing diagrams (Figs. 2, 4 and 6), for complex **6**, there are two inter-molecular S···S interactions (0.3361 and 0.3494 nm). For complex **5**, the interaction is more complex, having five interactions 0.3424, 0.3488, 0.3579, 0.3619 and 0.3716 nm, involving both inter- and intra-molecular interactions. For complex **4**, perhaps due to the stereochemical constraints mentioned above, no such interaction was observed. This interaction has been explained in terms of ligand close-packing by the fact that an S atom has a non-cylindrical electron density distribution as a result of the presence of two lone electron pairs,[23,24] which makes the effective ligand radius, and hence S···S, a function of orientation.

Examination of the structures of Sn(IV) complexes containing an *N*-donor atom and test results of antitumour activity revealed that in the active Sn complexes the average Sn—N bond lengths are > 0.239 nm, whereas the inactive complexes have Sn—N bonds < 0.239 nm, which implies 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.[26] From Table 2 we can see that the Sn···N bond lengths are all longer than 0.239 nm, and the results of bioactivity measurements show that complexes **4**, **5** and **6** all have antitumour activity against culture cells, which is in accordance with the correlation of Sn—N bond length with antitumour activity.

Supplementary data

Atomic coordinates, thermal parameters and bond lengths and angles for complexes **4**, **5** and **6** have been deposited at the Cambridge Crystallographic Data Center. CCDC nos. CCDC 192495, 183603, 192508. 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), quoting the deposition numbers for **4**, **5** and **6**, respectively.

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