X-ray structural study on spirocyclic bis(ethane-1,2-dithiolato[2−]-*S*,*S*′)tin(IV) and its pyridine and 2-(2-pyridyl)ethylamine adducts

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Abstract

Spirocyclic bis(ethane-1,2-dithiolato[2−]-*S*,*S*′)tin(IV) forms hexacoordinate crystalline complexes with pyridine and 2-(2-pyridyl)ethylamine. The compounds have been prepared by conventional methods and the crystal structures have been determined by an X-ray diffraction study. In the parent compound the tin is tetracoordinate in a highly distorted tetrahedral structure, with a weak intermolecular Sn···S interaction. On the contrary, the adducts are essentially octahedral about the tin, with longer Sn–S bonds in the five-membered rings SnS_2C_2. The 2-(2-pyridyl)ethylamine ligand is bonded to the metal through the aminic nitrogen.

Introduction

The coordination of spirocyclic bis(dithiolato)tin(IV) compounds with N- and O-donor ligands has been described by several authors [1]. The acceptor ability of the tin and the structures of the complexes, in comparison with those of the corresponding tin(IV) tetrahalides, have been studied. The formation of (i) neutral hexacoordinated adducts with Lewis bases [2, 3] and (ii) anionic pentacoordinated complexes with tetralkylammonium halides [4] has been well established. The latter have been characterized by ^{1}H NMR and ^{119}Sn Mössbauer spectroscopy [4], and the crystal structure of $[(CH_3)_4]^+[(C_7H_6S_2)SnCl]^-$ has been reported [5]. The former class of compounds has been studied earlier by means of IR, ^{1}H NMR and Mössbauer spectroscopy [2–4, 6, 7]. Normally *trans*- and *cis*- octahedral configurations have been attributed to complexes with mono- and bidentate ligands, respectively. The molecular structure of the 2,2′-bipyridine adduct of benzenetetrathiolatotin(IV) has been determined [8], but crystal structure studies on *trans*- and *cis*-octahedral adducts of spirocyclic tetrathiolatotin(IV) have not been made. We report here the crystal structures of bis(ethanedithiolato[2−]-*S*,*S*′)tin(IV) (I) and its adducts with pyridine, *trans*-bis(ethanedithiolato[2−]-*S*,*S*′)bis(pyridine)tin(IV) (II). We have also considered the formation of adducts with the potentially bidentate ligand 2-(2-pyridyl)ethylamine, in view of the reported observation of antitumor activity of some of its complexes with metal [9] and organometal [10] compounds. Thus the 1:2 complex, *trans*-bis(ethanedithiolato[2−]-*S*,*S*′)bis(2-[2-pyridyl]ethylamine)tin(IV) (III), was obtained and its crystal structure determined.

Experimental

Compounds **I** and **II** were synthesized following the procedures of ref. 6. The adduct **III** was obtained as a crystalline solid on recrystallizing **I** from hot 2-(2-pyridyl)ethylamine. This compound has not been described previously.

I: m.p. 178 °C (lit. [6] 180–183 °C); *Anal.* Calc. for $C_4H_8S_4Sn$: C, 15.85; H, 2.66. Found: C, 15.8; H, 2.6%.

II: m.p. 172 °C; *Anal.* Calc. for $C_{14}H_{18}N_2S_4Sn$: C, 36.45; H, 3.93; N, 6.07; Found: C, 36.2; H, 3.7; N, 5.9%.

III: m.p. 163 °C; *Anal.* Calc. for $C_{18}H_{28}N_4S_4Sn$: C, 39.50; H, 5.15; N, 10.23; Found: C, 38.7; H, 5.0; N, 9.6%.

The IR and far-IR spectra were recorded on a Nicolet 5SXC and a FAR 20F vacuum spectrometer, respectively. IR relevant bands: ν_{as}(Sn–S) at 328 (**I**), 312 (**II**) and 306 (**III**) cm^{-1}; ν_s(Sn–S) at 385 (**I**), 340 (**II**) and 338 (**III**) cm^{-1}, attributed according to ref. 3; ν(Sn–N) at 222 (**II**) and 233 (**III**) cm^{-1} tentatively attributed referring to SnX_4L_2 complexes (X = Cl, Br; L = pyridine,

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γ-picoline, and 4-tert-butylpyridine) [11]; $\nu(NH_2)$ (**III**) at 3280 and 3190 cm^{-1}, straightforward assignment.

Crystallography

Crystals of **I** and **III**, in the form of regularly shaped parallelepipeds were grown from a dichloromethane solution. A crystal of good quality for **II** was obtained by cutting a larger crystal and directly inserting it in a quartz capillary previously filled with vaseline/petrolatum (OBAT-55 Rol Oil), because of its sensitivity to air and moisture. These operations were carried out in a glove box in an oxygen- and moisture-free nitrogen atmosphere. Details of crystal data, measurement of intensity, data processing and refinement procedure are given in Table 1. Throughout data collection, crystal **II** was thought triclinic and so the collected reflections were twice as necessary. An empirical absorption correction, based on measurements of eight reflections at $\chi=270°$ for different azimuthal angles (Ψ-scan), was made. During the refinement of the three structures it was observed that a hundred of the weakest intensity reflections exhibited relatively poor agreement with the calculated structure factors, and in all cases $F_o \gg F_c$. Since this effect was clearly systematic, these low-intensity data were omitted from further refinement cycles, as well as those severely suffering from extinction. The largest peaks on the final difference maps were close to the Sn atoms. Fractional atomic coordinates

TABLE 1. Structure determination summary

Crystal data			
Empirical formula	$C_4H_8S_4Sn$	$C_{14}H_{18}N_2S_4Sn$	$C_{18}H_{28}N_4S_4Sn$
Color; habit		transparent colorless parallelopipeds	
Crystal size (mm)	0.30×0.35×0.50	0.15×0.25×0.45	0.35×0.30×0.40
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pccn*	*C2/c*	$P2_1/c$
Unit cell dimensions			
a (Å)	13.841(2)	13.526(6)	10.450(2)
b (Å)	7.705(8)	8.881(6)	11.744(2)
c (Å)	8.656(8)	15.998(10)	9.163(2)
β (°)		110.72(7)	92.33(2)
Volume ($Å^3$)	923.1(2.0)	797.4(1.6)	1123.7(4)
Z	4	4	2
Formula weight	303.0	461.2	547.4
Density (calc.) (Mg/m^3)	2.180	1.704	1.618
Absorption coefficient (mm^{-1})	3.6	1.9	1.5
F(000)	584	920	556
Data collection			
Diffractometer used		Siemens R3m/V	
Radiation		Mo Kα (λ=0,71073 Å)	
Temperature (K)		294	
Monochromator		highly oriented graphite crystal	
2θ Range (°)	4.0–55.0	4.0–45.0	4.0–55.0
Scan type		ω–2θ	
Scan speed		variable; 4.51 to 14.65°/min in ω	
Scan range (ω)	0.80°+Kα-separation	0.60°+Kα-separation	0.70°+Kα-separation
Background measurement		stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time	
Reflections collected	1267	2470	2870
Independent reflections	1068	1185 ($R_{int}=5.08\%$)	2595 ($R_{int}=2.72\%$)
Observed reflections ($F>4.0\sigma(F)$)	895	1012	2004
Solution and refinement			
System used		Siemens SHELXTL PLUS (Release 4.1) (1987)	
Solution		direct methods	
Refinement method		full-matrix least-squares	
Quantity minimized		$\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2$	
Hydrogen atoms		Riding model, common variable isotropic *U*	
Weighting scheme	$w^{-1}=\sigma^2(F)+0.0107F^2$	$w^{-1}=\sigma^2(F)+0.0077F^2$	$w^{-1}=\sigma^2(F)+0.0022F^2$
No. parameters refined	43	98	125
Final *R* indices (obs. data) (%)	$R=4.49$, $R_w=6.07$	$R=4.68$, $R_w=6.32$	$R=2.99$, $R_w=4.58$
Goodness-of-fit	0.68	0.68	0.82
Data-to-parameter ratio	20.8:1	10.3:1	16.0:1
Largest difference peak (e $Å^{-3}$)	1.34	0.68	0.70
Largest difference hole (e $Å^{-3}$)	−2.39	−1.50	−0.89

and equivalent thermal parameters are given in Table 2, while bond distances and angles are listed in Table 3. See also 'Supplementary material'.

Results and discussion

The preparation procedure employed, with a large excess of ligand as solvent, affords the 1:2 adducts of **I**. Even 2-(2-pyridyl)ethylamine, which acts as bidentate in the metal and organometal complexes previously described (see for example refs. 9, 10 and 12), behaves as monodentate and binds through the aminic nitrogen. In fact it was shown that the stability constants of aminic complexes of bis(ethane-1,2-dithiolato)tin(IV) in benzene solution are higher than those of the pyridinic one [13]. The IR spectrum of **III** shows sharp N–H stretching bands at considerably lower values (3280 and 3190 cm^{-1} versus about 3390 and 3300 cm^{-1} [14],

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*[a]
I				
Sn	2500	2500	2326(1)	28(1)
S(1)	2666(1)	−166(2)	3708(3)	40(1)
S(2)	3994(1)	2114(3)	981(2)	41(1)
C(1)	3704(6)	−933(10)	2585(8)	60(2)
C(2)	4416(6)	345(13)	2131(10)	63(3)
II				
Sn	0	0	0	26(1)
S(1)	934(2)	−343(3)	−1058(1)	42(1)
S(2)	−27(1)	−2758(2)	172(1)	42(1)
N	1664(5)	211(6)	1195(4)	36(2)
C(1)	810(7)	−2346(9)	−1178(6)	68(4)
C(2)	936(6)	−3190(9)	−351(6)	68(4)
C(3)	1815(6)	−409(10)	2003(5)	44(3)
C(4)	2726(8)	−251(11)	2702(6)	57(4)
C(5)	3553(5)	582(10)	2591(5)	49(3)
C(6)	3408(5)	1173(8)	1765(5)	44(3)
C(7)	2463(5)	939(7)	1088(4)	39(2)
III				
Sn	0	0	0	26(1)
S(1)	1810(1)	−1316(1)	471(1)	37(1)
S(2)	−479(1)	−101(1)	2623(1)	38(1)
N(1)	1349(3)	1562(2)	647(3)	33(1)
N(2)	3616(3)	4008(3)	−1946(3)	40(1)
C(1)	1452(5)	−1738(4)	2321(5)	62(2)
C(2)	955(5)	−855(4)	3273(4)	55(1)
C(3)	2272(3)	2042(3)	−357(4)	39(1)
C(4)	2976(4)	3077(3)	256(4)	41(1)
C(5)	4004(3)	3503(3)	−699(3)	31(1)
C(6)	5289(4)	3408(3)	−299(4)	46(1)
C(7)	6204(4)	3839(3)	−1180(5)	48(1)
C(8)	5817(4)	4373(3)	−2447(5)	49(1)
C(9)	4528(4)	4433(4)	−2783(4)	48(1)

[a]Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond lengths (Å) and angles (°)

I	
Sn–S(1)	2.388(2)
Sn–S(2)	2.391(2)
S(1)–C(1)	1.833(8)
S(2)–C(2)	1.786(10)
C(1)–C(2)	1.448(12)
S(1)–Sn–S(2)	93.1(1)
S(1)–Sn–S(1A)	119.9(1)
S(2)–Sn–S(1A)	115.7(1)
S(2)–Sn–S(2A)	121.7(1)
Sn–S(1)–C(1)	95.0(3)
Sn–S(2)–C(2)	96.1(3)
S(1)–C(1)–C(2)	117.3(6)
S(2)–C(2)–C(1)	116.6(6)
II	
Sn–S(1)	2.463(3)
Sn–S(2)	2.467(3)
Sn–N	2.390(6)
S(1)–C(1)	1.791(8)
S(2)–C(2)	1.821(11)
N–C(3)	1.353(11)
N–C(7)	1.321(10)
C(1)–C(2)	1.477(13)
C(3)–C(4)	1.347(11)
C(4)–C(5)	1.404(14)
C(5)–C(6)	1.369(11)
C(6)–C(7)	1.367(8)
S(1)–Sn–S(2)	89.2(1)
S(1)–Sn–N	89.6(2)
S(2)–Sn–N	92.1(1)
S(2)–Sn–S(1A)	90.8(1)
N–Sn–S(1A)	90.4(2)
N–Sn–S(2A)	87.9(1)
Sn–S(1)–C(1)	98.3(4)
Sn–S(2)–C(2)	96.7(3)
Sn–N–C(3)	120.9(5)
Sn–N–C(7)	121.2(5)
C(3)–N–C(7)	117.9(6)
S(1)–C(1)–C(2)	115.6(6)
S(2)–C(2)–C(1)	115.5(6)
N–C(3)–C(4)	122.4(9)
C(3)–C(4)–C(5)	119.0(9)
C(4)–C(5)–C(6)	118.4(6)
C(5)–C(6)–C(7)	118.7(7)
N–C(7)–C(6)	123.4(7)
III	
Sn–S(1)	2.467(1)
Sn–S(2)	2.478(1)
Sn–N(1)	2.374(3)
S(1)–C(1)	1.819(4)
S(2)–C(2)	1.820(5)
N(1)–C(3)	1.472(5)
N(2)–C(5)	1.335(4)
N(2)–C(9)	1.343(5)
C(1)–C(2)	1.463(6)
C(3)–C(4)	1.516(5)
C(4)–C(5)	1.498(5)
C(5)–C(6)	1.382(5)
C(6)–C(7)	1.374(6)
C(7)–C(8)	1.366(6)
C(8)–C(9)	1.372(6)

(continued)

TABLE 3. (*continued*)

III	
S(1)–Sn–S(2)	89.1(1)
S(1)–Sn–N(1)	89.8(1)
S(2)–Sn–N(1)	86.3(1)
S(2)–Sn–S(1A)	90.9(1)
N(1)–Sn–S(1A)	90.2(1)
N(1)–Sn–S(2A)	93.7(1)
Sn–S(1)–C(1)	98.5(2)
Sn–S(2)–C(2)	98.3(1)
Sn–N(1)–C(3)	122.5(2)
C(5)–N(2)–C(9)	117.1(3)
S(1)–C(1)–C(2)	117.0(3)
S(2)–C(2)–C(1)	117.2(3)
N(1)–C(3)–C(4)	113.3(3)
C(3)–C(4)–C(5)	113.6(3)
N(2)–C(5)–C(4)	116.6(3)
N(2)–C(5)–C(6)	121.4(3)
C(4)–C(5)–C(6)	122.0(3)
C(5)–C(6)–C(7)	120.4(4)
C(6)–C(7)–C(8)	118.7(4)
C(7)–C(8)–C(9)	117.9(4)
N(2)–C(9)–C(8)	124.5(4)

respectively) than the free ligand, which presents a N–H IR pattern typical of a remarkable extent of hydrogen bonding. The formation of 1:1 adducts with monodentate ligands has been demonstrated by calorimetric titrations [13], but such kind of products have not yet been isolated.

The three structures consist of discrete, monomeric tin(IV) complexes (Fig. 1). There are no unusually short intermolecular contacts between the monomers. The shortest contacts between tin and the ethane bridge carbon atoms are 3.13, 3.23 and 3.28 Å in **I**, **II** and **III**, respectively and a moderately short Sn···S(1) at $(x, \frac{1}{2}-x, z-\frac{1}{2})$ of 3.75 Å is present only in **I**. In crystal **I** the coordination at the Sn(IV) atom can be described as highly distorted tetrahedral (pertinent angles from 93.1 to 121.7°), while in **II** and **III** the coordination is essentially octahedral, although most of the bond angles at the tin differ somewhat from the ideal octahedral *cis* value of 90°, falling between 87.9 and 93.7°. In the three complexes the conformation of the five-membered ring is close to the twist-envelope (C_2) symmetry, as shown by the torsion angles and the atomic displacements from the mean SnS_2C_2 plane (Table 4), with C(2) displaced by 0.56 (**I**), 0.61 (**II**) and 0.52 (**III**) Å from the approximate plane of the other four atoms. The situation parallels that found, for instance, in 2,2-dimethyl-1,3-dithia-2-stannolane [16] and in 2-chloro-2-n-butyl-1,3-dithia-2[1,10-phenanthroline] stannolane [17] and thus confirms the Sn–S stretching IR absorption assignment to the pattern of bands observed in the 300–400 cm^{-1} region, very similar in this kind of compound. In **I** the two five-membered rings are at 78.5°, while in **II** and **III** this angle is crystallographically imposed to 0°, the structures being centrosymmetric at the tin atom. Moreover, in **II** the pyridine rings at the apical positions are virtually normal (94.1°) to the equatorial plane, while in **III** the dihedral angle between the pyridine rings, far from the inner core, and the

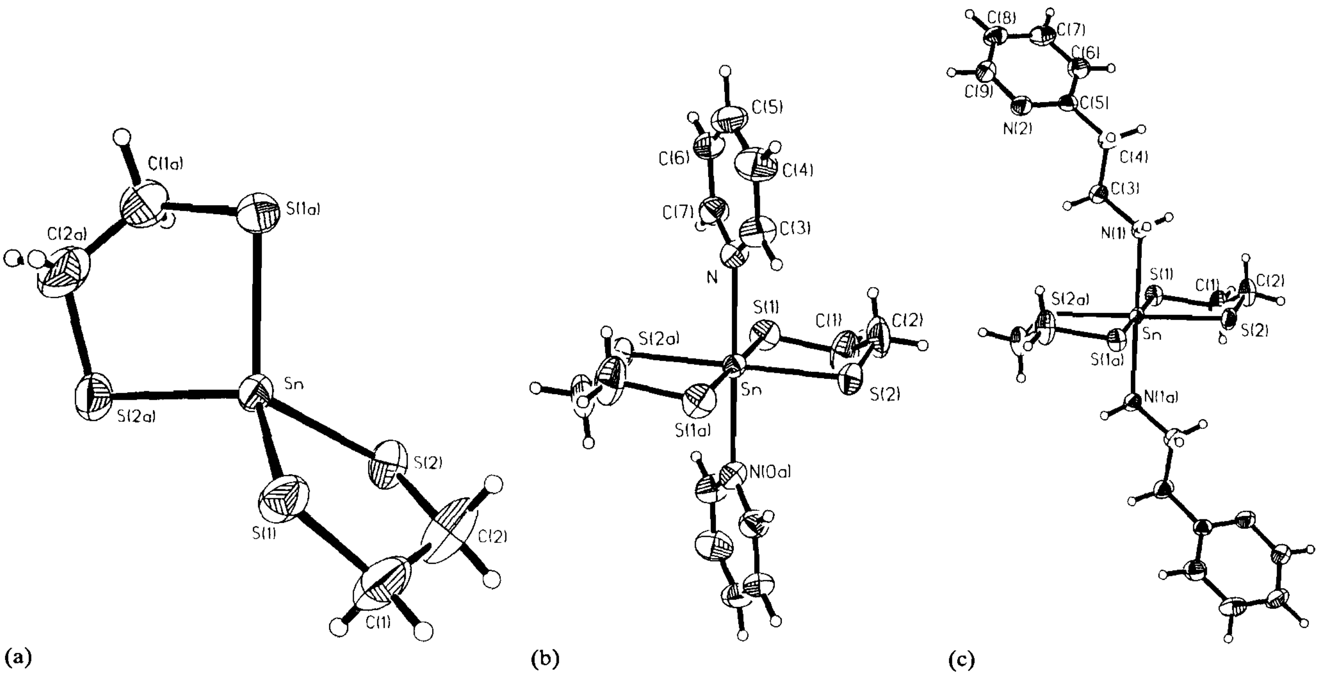

Fig. 1. ORTEP plots of **I** (a), **II** (b) and **III** (c) complexes with thermal ellipsoids at the 50% probability level and with atomic labeling. Hydrogen atoms are represented by spheres of arbitrary size.

TABLE 4. Conformation of the five-membered SnS_2C_2 ring. Deviation (Å) from the mean SnS_2C_2 ring

Atom	I	II	III	C_2[a]
Sn	0.01	0.02	0.00	0
S(1)	0.10	0.09	0.11	0.18
S(2)	−0.12	−0.15	−0.10	−0.18
C(1)	−0.28	−0.30	−0.28	−0.29
C(2)	0.29	0.32	0.27	0.29
Pertinent torsion angles (°)				
Sn–S(1)–C(1)–C(2)	−38.2	−39.3	−38.0	−39
S(1)–C(1)–C(2)–S(2)	58.8	61.5	55.7	48
C(1)–C(2)–S(2)–Sn	−39.7	−43.3	−37.2	−39
C(2)–S(2)–Sn–S(1)	11.6	13.8	9.8	15
S(2)–Sn–S(1)–C(1)	9.6	9.1	10.7	15

[a]Ref. 15.

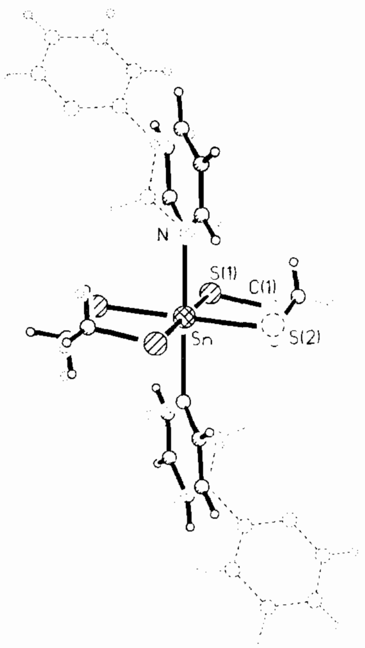

Fig. 2. Superimposition of **II** (——) with **III** (– – –).

equatorial plane is 42.8°. The relative disposition of the ethylamine chains of **III** defines a fully extended arrangement of the apical N-donor ligands, Sn–N(1)–C(3)–C(4) and N(1)–C(3)–C(4)–C(5) torsion angles being 176.7 and 174.6°, respectively. The structural consequences of introducing in the tetrahedral complex **I** the two N-donor ligands, so affording the octahedral complexes **II** and **III**, results in a lengthening of the Sn–S bond distances (from a mean value of 2.390 Å in **I** to 2.465 Å in **II** and 2.473 Å in **III**) accomplished by a narrowing of the S–Sn–S bite angle (from 93.1° in **I** to 89.2° in **II** and 89.1° in **III**). Correspondingly the IR ν_s(Sn–S) is found in **I** at 45 and 47 cm^{-1} higher than in **II** and **III**, respectively. Superimposition [18] of the common equatorial plane of **II** with **III** (Fig. 2) shows a weighted r.m.s. deviation of only 0.04 Å, confirming that the inner core of the coordination sphere is practically superimposable.

The bond lengths conform with those of similar compounds and there are some moderate differences in bond angles which may be ascribed to packing effects and intermolecular strain. In particular, the Sn–N distances (2.390 Å in **II** and 2.374 Å in **III**) are similar to distances observed in other octahedral tin(IV) complexes, for instance in 2-chloro-2-n-butyl-1,3-dithia-2-[1,10-phenanthroline]stannolane (2.39 and 2.40 Å) [17], diphenyltin-dichloride-2,2′-bipyridine (2.34 and 2.37 Å) [19], di-n-butyltin-dichloride-1,10-phenanthroline (2.35 and 2.43 Å) [20], di-*p*-tolyltin-dichloride-2,2′-bipyridine (2.31 and 2.37 Å) [21], diphenyltindi-isothiocyanate-2,2′-bipyridine (2.33 and 2.34 Å) [22], and in all-*trans*-octahedral complexes of the type $SnR_2Cl_2 \cdot 2L$ (R = CH_3, L = *N*-methylimidazole, 2.33 Å [23]; L = 3,5-dimethylpyrazole, 2.38 Å [24]; L = pyridine, 2.39 Å [25]; L = pyrazole, 2.34 [26]; R = CH_2=CH, L = pyrazole, 2.32 Å [27]). In any cases they significantly exceed the sum of the atomic radii of tin and nitrogen (2.10 Å [28]) and no significant difference was observed between the Sn–N(pyridine) (in **II**) and Sn–N(amine) (in **III**) bond distances. The Sn–S bonds (mean value of 2.465 Å in **II** and 2.472 Å in **III** are in agreement with a covalent radii sum of 2.44 Å [29], and with a number of values reported for Sn(IV) thiolate complexes [17, 29–34].

Supplementary material

Additional data, including anisotropic temperature factors (Table S1), hydrogen atoms coordinates (Table S2), and a listing of observed/calculated structure factors (Table S3), as well as the packing diagrams (Fig. S1), are available from the authors.

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