Tautomerism in coordinated 1-phenyl-5-thione-1,2,3,4-tetrazole (HL) Synthesis and crystal structure of [SnMe₂(phen)L₂] (phen = 1,10-phenanthroline)

J. Bravo [a], M.B. Cordero [a], J.S. Casas [b], M.V. Castaño [b,*], A. Sánchez [b], J. Sordo [b]

[a] *Departamento de Química Pura y Aplicada, Universidade de Vigo, 36200 Vigo, Spain*
[b] *Departamento de Química Inorgánica, Universidade de Santiago de Compostela, 15706 Santiago de Compostela, Spain*

Abstract

The compound [SnMe₂(phen)L₂] (phen = 1,10-phenanthroline) was prepared by reaction of a mixture of 1-phenyl-5-thione-1,2,3,4-tetrazole, phen and SnMe₂O in 2:1:1 mole ratio in refluxing methanol. The structure of the complex was determined by X-ray diffraction. The unit cell contains two independent molecules. In one, the tin atom is coordinated to the methyl groups, to a bidentate phen and to two N(4)-bound L⁻, one of which also forms an additional Sn ⋯ S secondary bond. In the other independent molecule, the metal atom is coordinated to the methyl groups, to a bidentate phen and to one N- and one S-bound L⁻ which also forms an additional Sn ⋯ N secondary bond. Thus the two independent molecules are formally linkage isomers. The IR spectrum was recorded and a multinuclear NMR study was carried out.

Keywords: Tin; Tautomerism; X-ray structure; Thionetetrazoles; Complexes

1. Introduction

The coordination of 1-substituted-5-thione tetrazoles to organotin(IV) cations has been the subject of some controversy in recent years. In solution these compounds exist in two tautomeric forms.
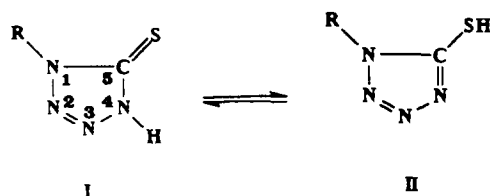
When they react with metallic or organometallic cations under suitable conditions, they afford either *N*- or *S*-bound complexes. When the first complex from 1-phenyl-5-thione-1,2,3,4-tetrazole (HL) and triphenyltin(IV) was prepared [1], *N*-coordination was assumed. Later, several X-ray diffraction studies of dibutyl-, trib-

utyl-, triphenyl- and trimethyl-tin(IV) complexes showed primary *S*-coordination [2]. In this work we have found both *N*- and *S*-coordination in crystals of [SnMe₂(phen)L₂].

2. Experimental section

2.1. Reagents

HL (Ega Chemie), phen (Aldrich) and dimethyltin-(IV) oxide (Alfa) were used as supplied.

2.2. Synthesis of [SnMe₂(phen)L₂] and physicochemical measurements

HL (1.000 g, 5.6 mmol) and phen (0.556 g, 2.8 mmol) were dissolved in methanol (ca. 100 ml). Solid SnMe₂O (0.462 g, 2.8 mmol) was added to form a suspension that was stirred under reflux for 24 h, after which the resulting solution was concentrated in vacuo to give an orange solid which was filtered off and dried under vacuum. M.p. 175°C. Anal. Calc. for C₂₈H₂₄N₁₀S₂Sn, C 49.2, H 3.5, N 20.5; found, C 48.9,

* Corresponding author.

Table 1
Positional parameters for [SnMe$_2$(phen)L$_2$]

Atom	x	y	z	B (Å^2)
Sn(1)	0.16091(8)	0.39210(6)	0.15199(8)	2.64(2)
Sn(2)	0.67661(8)	0.90324(6)	0.22817(8)	2.61(2)
S(1)	0.2855(4)	0.4598(3)	0.4155(4)	4.9(1)
S(2)	0.2600(3)	0.4208(3)	−0.1164(4)	3.59(9)
S(3)	0.7840(4)	1.0673(3)	0.3124(4)	4.2(1)
S(4)	0.7295(3)	0.8812(3)	−0.0751(4)	3.71(9)
N(1)	0.3434(9)	0.6230(7)	0.397(1)	3.1(3)
N(2)	0.329(1)	0.6654(8)	0.322(1)	3.8(3)
N(3)	0.276(1)	0.6102(8)	0.240(1)	3.8(3)
N(4)	0.254(1)	0.5334(8)	0.259(1)	3.3(3)
N(5)	0.1650(9)	0.5577(8)	−0.058(1)	3.0(3)
N(6)	0.106(1)	0.5890(8)	0.020(1)	3.3(3)
N(7)	0.0957(9)	0.5392(8)	0.079(1)	3.2(3)
N(8)	0.1458(9)	0.4741(8)	0.043(1)	2.8(3)
N(9)	0.118(1)	0.2557(8)	0.200(1)	3.4(3)
N(10)	0.0616(9)	0.2833(8)	0.011(1)	2.9(3)
N(11)	0.898(1)	1.0991(9)	0.507(1)	3.6(3)
N(12)	0.920(1)	1.054(1)	0.576(1)	5.0(4)
N(13)	0.869(1)	0.9783(9)	0.537(1)	5.1(4)
N(14)	0.814(1)	0.9708(9)	0.444(1)	4.3(4)
N(15)	0.6435(9)	1.0235(8)	−0.032(1)	3.1(3)
N(16)	0.596(1)	1.0701(8)	0.052(1)	3.8(3)
N(17)	0.597(1)	1.0343(8)	0.126(1)	3.7(3)
N(18)	0.6435(9)	0.9645(7)	0.098(1)	2.9(3)
N(19)	0.6484(9)	0.7802(8)	0.311(1)	3.0(3)
N(20)	0.5672(9)	0.7804(7)	0.113(1)	2.7(3)
C(1)	0.296(1)	0.541(1)	0.358(1)	3.3(3) *
C(2)	0.400(1)	0.669(1)	0.498(1)	3.2(3) *
C(3)	0.451(1)	0.626(1)	0.552(1)	4.0(3) *
C(4)	0.508(1)	0.672(1)	0.649(2)	4.8(4) *
C(5)	0.515(2)	0.758(1)	0.688(2)	6.0(5) *
C(6)	0.463(2)	0.800(1)	0.637(2)	6.0(5) *
C(7)	0.406(1)	0.757(1)	0.537(2)	4.8(4) *
C(8)	0.192(1)	0.4852(9)	−0.044(1)	2.7(3) *
C(9)	0.191(1)	0.6049(9)	−0.132(1)	3.0(3) *
C(10)	0.213(1)	0.564(1)	−0.234(1)	4.0(3) *
C(11)	0.235(2)	0.615(1)	−0.304(2)	5.3(4) *
C(12)	0.233(2)	0.701(1)	−0.272(2)	5.2(4) *
C(13)	0.209(2)	0.739(1)	−0.173(2)	5.3(4) *
C(14)	0.186(1)	0.693(1)	−0.097(1)	3.8(3) *
C(15)	0.289(1)	0.351(1)	0.118(1)	3.5(4)
C(16)	0.052(1)	0.430(1)	0.247(1)	4.1(4)
C(17)	0.152(1)	0.242(1)	0.292(1)	4.3(4) *
C(18)	0.116(1)	0.167(1)	0.321(2)	4.7(4) *
C(19)	0.044(1)	0.109(1)	0.253(1)	4.1(4) *
C(20)	0.008(1)	0.122(1)	0.157(1)	3.5(3) *
C(21)	−0.064(1)	0.061(1)	0.083(1)	4.0(3) *
C(22)	−0.092(1)	0.075(1)	−0.014(1)	3.9(3) *
C(23)	−0.049(1)	0.148(1)	−0.042(1)	3.3(3) *
C(24)	−0.076(1)	0.160(1)	−0.142(1)	3.5(3) *
C(25)	−0.032(1)	0.234(1)	−0.163(1)	3.8(3) *
C(26)	0.035(1)	0.294(1)	−0.084(1)	3.3(3) *
C(27)	0.019(1)	0.2102(9)	0.032(1)	2.6(3) *
C(28)	0.050(1)	0.1965(9)	0.133(1)	2.8(3) *
C(31)	0.833(1)	1.046(1)	0.424(1)	3.3(3) *
C(32)	0.942(1)	1.187(1)	0.530(1)	4.0(3) *
C(33)	1.033(1)	1.211(1)	0.576(2)	4.9(4) *
C(34)	1.075(2)	1.299(1)	0.603(2)	6.2(5) *
C(35)	1.026(2)	1.356(2)	0.578(2)	7.8(7) *
C(36)	0.932(2)	1.332(2)	0.538(2)	9.0(8) *
C(37)	0.885(2)	1.242(2)	0.513(2)	6.8(6) *
C(38)	0.674(1)	0.9576(9)	−0.003(1)	3.0(3) *

Table 1 (continued)

Atom	x	y	z	B (Å^2)
C(39)	0.659(1)	1.053(1)	−0.126(1)	3.2(3) *
C(40)	0.662(1)	0.995(1)	−0.227(1)	4.0(3) *
C(41)	0.678(1)	1.029(1)	−0.316(2)	4.9(4) *
C(42)	0.688(2)	1.114(1)	−0.302(2)	5.3(4) *
C(43)	0.686(1)	1.170(1)	−0.203(2)	5.0(4) *
C(44)	0.669(1)	1.140(1)	−0.110(1)	4.1(3) *
C(45)	0.572(1)	0.946(1)	0.326(1)	4.1(4)
C(46)	0.798(1)	0.849(1)	0.180(1)	3.6(4)
C(47)	0.523(1)	0.7787(9)	0.018(1)	3.0(3) *
C(48)	0.460(1)	0.710(1)	−0.049(1)	3.6(3) *
C(49)	0.437(1)	0.638(1)	−0.019(1)	3.5(3) *
C(50)	0.481(1)	0.635(1)	0.081(1)	3.1(3) *
C(51)	0.462(1)	0.561(1)	0.118(1)	3.4(3) *
C(52)	0.505(1)	0.561(1)	0.214(1)	3.6(3) *
C(53)	0.568(1)	0.633(1)	0.282(1)	3.2(3) *
C(54)	0.614(1)	0.636(1)	0.381(1)	4.2(4) *
C(55)	0.671(1)	0.709(1)	0.445(2)	4.8(4) *
C(56)	0.689(1)	0.781(1)	0.406(1)	4.3(4) *
C(57)	0.589(1)	0.7086(9)	0.249(1)	2.6(3) *
C(58)	0.545(1)	0.7082(9)	0.145(1)	2.4(2) *

$B = 4/3\Sigma_{ij}\mathbf{B}_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$. Starred atoms were refined isotropically.

H 3.6, N 21.0%. Elemental analysis was performed with a Carlo Erba 1108 microanalyzer. IR spectra were recorded in KBr pellets and Nujol mulls on a Mattson FT-IR Cygnus 100 spectrometer. ^{1}H (300.135 MHz) and proton decoupled ^{13}C (75.476 MHz) spectra were recorded on a Bruker AMX300 spectrometer; ^{119}Sn (186.456 MHz) spectra were recorded on a Bruker AMX500 apparatus. Samples were disolved in CDCl$_3$ (in tubes of 5 mm outside diameter) at room temperature and spectra were referenced to the solvent signal (1H, 7.27 ppm; ^{13}C, 77.00 ppm) and external pure Sn(CH$_3$)$_4$.
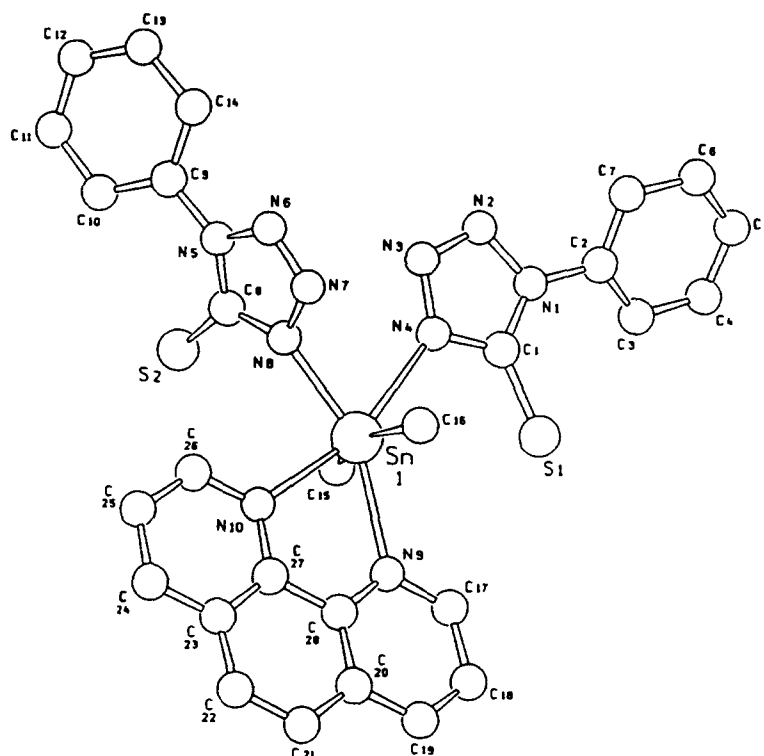

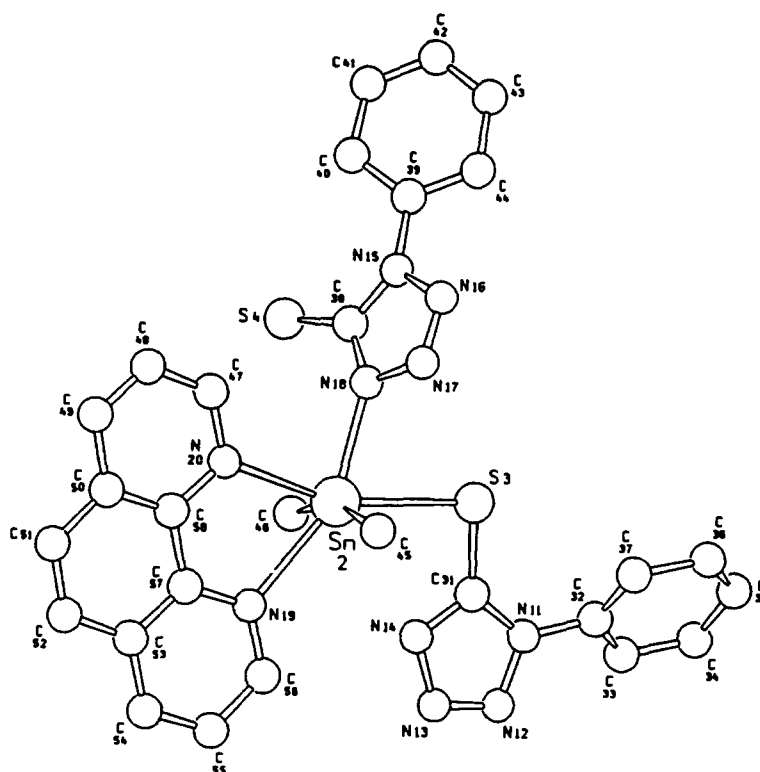Fig. 1. Perspective view showing the atom numbering scheme in [Sn(1)Me$_2$(phen)L$_2$].

Fig. 2. Perspective view showing the atom numbering scheme in [Sn(2)Me$_2$(phen)L$_2$].

2.3. Crystal structure determination

Crystal data. C$_{28}$H$_{24}$N$_{10}$S$_2$Sn; M = 683.4; triclinic, space group P$\bar{1}$ (N° 2), a = 14.398(2), b = 16.4706(9), c = 12.8364(9) Å, α = 107.043(5), β = 93.126(7), γ = 98.846(7)°, U = 2859.7 Å^3 (by least squares refinement of setting angles for 25 automatically centred reflections), Z = 4 with two independent molecules per asym-

metric unit, D_c = 1.587 g cm^{-3}, μ = 10.725 cm^{-1}, crystal dimensions 0.06 × 0.05 × 0.06 mm^3.

Data collection and processing. Enraf-Nonius CAD-4 diffractometer, λ(Mo Kα) = 0.71073 Å, $\omega/2\Theta$ mode, range $-18 < h < 18$, $-21 < k < 21$, $-16 < l < 16$, 3° $< \theta < 27$°, 24 860 reflections measured, 12 415 unique (R_{int} = 0.048) and 6841 with $I > 3\sigma(I)$, $F(000)$ = 1376; Lorentz and polarization corrections [3]. Absorp-

Table 2
Bond distances and angles around the Sn atoms

	Distance (Å)		Angle (deg)
[Sn(1)Me$_2$(phen)L$_2$]			
Sn(1)–N(4)	2.463(4)	N(4)–Sn(1)–N(8)	76.7(1)
Sn(1)–N(8)	2.233(4)	N(4)–Sn(1)–N(9)	131.0(1)
Sn(1)–N(9)	2.500(4)	N(8)–Sn(1)–N(10)	84.5(1)
Sn(1)–N(10)	2.359(4)	N(9)–Sn(1)–N(10)	67.6(1)
Sn(1)–C(15)	2.090(5)	C(15)–Sn(1)–C(16)	156.6(3)
Sn(1)–C(16)	2.100(6)		
[Sn(2)Me$_2$(phen)L$_2$]			
Sn(2)–S(3)	2.772(1)	S(3)–Sn(2)–N(18)	78.0(1)
Sn(2)–N(18)	2.261(3)	S(3)–Sn(2)–N(19)	130.49(9)
Sn(2)–N(19)	2.540(3)	N(18)–Sn(2)–N(20)	84.2(1)
Sn(2)–N(20)	2.402(3)	N(19)–Sn(2)–N(20)	67.3(1)
Sn(2)–C(45)	2.096(5)	C(45)–Sn(2)–C(46)	159.5(2)
Sn(2)–C(46)	2.123(5)		

tion corrections were also applied at a later stage in refinement [3] (max., min. absorption corrections: 1.2020, 0.7349).

Structure analysis and refinement. The structure was determined by Patterson analysis and difference Fourier methods. The Sn, *S*, *N* and methyl C atoms were refined anisotropically and the other C atoms isotropically. A total of 480 parameters were refined. The H atoms were placed in calculated positions and their temperature parameters were fixed. Final *R* and *R'* values were 0.050 and 0.054 respectively. *S*(goof) = 2.94. The weighting scheme was $w^{-1} = \sigma^2(F_0)$. Programs used were SHELX76 [4] and SCHAKAL [5]. Scattering factors for non-H atoms were from Cromer and Mann [6], with corrections for anomalous dispersion from Cromer and Liberman [7]. The final atomic coordinates are listed in Table 1. Full tables of parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Crystal structure

Figs. 1 and 2 show the structures and numbering schemes of the two independent molecules in each asymmetric unit (hereafter referred to as [Sn(1)Me$_2$-(phen)L$_2$] and [Sn(2)Me$_2$(phen)L$_2$]). The interatomic
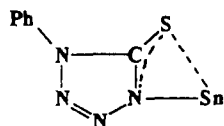
distances and angles around the tin atom are listed in Table 2.

In molecule [Sn(1)Me$_2$(phen)L$_2$], the tin atom is bound to the two methyl groups, to a bidentate phen and to two deprotonated *N*-bound tetrazole (L) molecules in a distorted octahedral arrangement with the methyl groups apical and the phen and L equatorial. Sn(1), N(4), N(8), N(9) and N(10) are almost coplanar ($\chi^2 =$ 8410), with Sn(1) deviating most from the best plane (by 0.0480(5) Å). Distortion from strict octahedral coordination is evident in several parameters. First, the Sn–N distances are not equal but range from 2.23 Å in the Sn(1)–N(8) bond (a value close to the sum of the covalent radii, 2.15 Å [8]), to 2.5 Å in the Sn(1)–N(9) bond. Secondly, the C(15)–Sn(1)–C(16) bond angle is just 156.6(3)°, and the equatorial bond angles range from 67.6(1)° to 131.0(1)°, with only N(8)–Sn(1)–N(10) approaching the ideal 90°. Whereas the acute N(9)–Sn(1)–N(10) angle is determined by the bite of phen, the wide N(4)–Sn(1)–N(9) angle and the length of the N(4)–Sn(1) and N(9)–Sn(1) bonds are determined by the equatorial plane [Sn(1), N(4), N(8), N(9) and N(10)] forming a dihedral angle of only 12.8(4)° with phen and being practically coplanar with the tetrazole ring N(1)–N(2)–N(3)–N(4)–C(1), which places the S(1) atom near the phen. The sub-90° angles N(4)–Sn(1)–N(8) and N(8)–Sn(1)–N(10) are made possible by the other tetrazole ring, N(5)–N(6)–N(7)–N(8)–C(8), adopting a position almost orthogonal to the equatorial plane (di-

Table 3
Bond distances and angles in the ligands

|	Distance (Å)		Angle (deg)
[Sn(1)Me$_2$(phen)L$_2$]			
S(1)–C(1)	1.695(5)	N(2)–N(1)–C(1)	109.3(4)
S(2)–C(8)	1.670(4)	N(1)–N(2)–N(3)	106.2(3)
N(1)–N(2)	1.370(5)	N(2)–N(3)–N(4)	110.8(4)
N(1)–C(1)	1.355(5)	N(3)–N(4)–C(1)	108.1(4)
N(2)–N(3)	1.287(5)	N(6)–N(5)–C(8)	109.7(3)
N(3)–N(4)	1.349(6)	N(5)–N(6)–N(7)	107.5(3)
N(4)–C(1)	1.343(6)	N(6)–N(7)–N(8)	110.2(4)
N(5)–N(6)	1.387(5)	N(7)–N(8)–C(8)	109.2(3)
N(5)–C(8)	1.371(5)		
N(6)–N(7)	1.262(5)		
N(7)–N(8)	1.365(5)		
N(8)–C(8)	1.371(5)		
[Sn(2)Me$_2$(phen)L$_2$]			
S(3)–C(31)	1.718(5)	N(12)–N(11)–C(31)	108.5(4)
S(4)–C(38)	1.669(5)	N(11)–N(12)–N(13)	106.1(4)
N(11)–N(12)	1.362(6)	N(12)–N(13)–N(14)	111.4(4)
N(11)–C(31)	1.365(6)	N(13)–N(14)–C(31)	106.6(4)
N(12)–N(13)	1.291(6)	N(16)–N(15)–C(38)	109.3(3)
N(13)–N(14)	1.364(6)	N(15)–N(16)–N(17)	106.7(4)
N(14)–C(31)	1.323(6)	N(16)–N(17)–N(18)	111.2(4)
N(15)–N(16)	1.412(5)	N(17)–N(18)–C(38)	108.4(3)
N(15)–C(38)	1.372(5)		
N(16)–N(17)	1.253(5)		
N(17)–N(18)	1.383(6)		
N(18)–C(38)	1.363(5)		

hedral angle 106.7(2)°). The coplanarity of the equatorial plane and the tetrazole ring N(1)–N(2)–N(3)–N(4)–C(1) may be due to an Sn(1) ··· S(1) interaction which places S(1) 3.523(5) Å from Sn(1) (a distance less than the sum of the van der Waals radii, 4.0 Å [9]) and formally increases the coordination number of the metal to seven. Bond distances and angles in the ligands are shown in Table 3.

The interatomic distances in both tetrazoles are as expected for the deprotonated thione form I (see Introduction), with short C–S bond lengths (close to that of a carbon–sulphur double bond in thioureas, 1.681 Å [10]) and one short [N(2)–N(3) and N(6)–N(7)] and two long [N(1)–N(2) and N(3)–N(4), and N(5)–N(6) and N(7)–N(8)] N–N bonds. Nevertheless, C(1)–S(1) is longer than C(8)–S(2) and C(1)–N(4) is shorter than C(8)–N(8), suggesting a rather greater shift of the S(1) tetrazole toward the thiol form and supporting the existence of S(1)–Sn(1) interaction.

In molecule [Sn(2)Me$_2$(phen)L$_2$] the tin atom is bound to the two methyl groups, to a bidentate phen and to one S- and one N-bound tetrazole (Fig. 2). As in [Sn(1)Me$_2$(phen)L$_2$], the equatorial atoms [Sn(2), N(18), N(19), N(20) and S(3)] are approximately coplanar, with the tin atom deviating most from the best plane (by about 0.05 Å). The C–Sn–C angle is wider and the Sn bonds longer than in [Sn(1)Me$_2$(phen)L$_2$] (Table 2). The Sn–S bond length (2.772(1) Å) is greater than those observed in the previously reported S-bound complexes of L with organotin(IV) compounds (2.48–2.61 Å [2]), and clearly exceeds the sum of the covalent radii (2.42 Å [8]). At the same time, the C(31)–S(3) bond

(1.718(5) Å) is shorter than a thiolate bond (1.808 Å [10]), probably because L, as in [Sn(1)Me$_2$(phen)L$_2$], is involved in pseudochelation, the Sn(2)–N(14) distance (3.12(1) Å) being well below the sum of the Van der Waals radii (3.75 Å [9]):
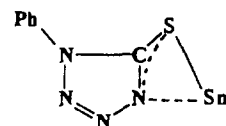
Although the tetrazoles S(1) and S(3) are both N,S-pseudobidentate rather than monodentate through different atoms (in one case the primary bond is Sn–N and in the other Sn–S), [Sn(1)Me$_2$(phen)L$_2$] and [Sn(2)Me$_2$-(phen)L$_2$] can be considered to be linkage isomers.

The intra-annular bond distances in the two tetrazole rings of [Sn(2)Me$_2$(phen)L$_2$] are in keeping with one being N-bound and the other primarily S-bound. Thus the C–N bonds of C(38) are of very similar lengths (1.372(5) and 1.365(6) Å), as corresponds to form I of the free tetrazole (see Introduction) while those of C(31) have clearly different lengths (1.323(6) and 1.365(6) Å), corresponding to form II.

3.2. IR study

The IR spectrum of the complex shows bands typical of coordinated phen [11]. The IR spectrum of free HL is essentially that previously described by Singh et al. [12], and the main shifts upon deprotonation and coordination can be summarized as follows.

(1) A group of bands present in HL at 3020(s) cm^{-1}, [ν(C–H) + ν(N–H)], 2898(s) cm^{-1}, 2750(s) cm^{-1}, [both ν(N–H)], and 2544(w) cm^{-1}, [ν(S–H), due to a minimal amount of thiol form] is replaced in the spectrum of the complex by a weak band at 3061 cm^{-1}, in keeping with the occurrence of the deprotonation.

Table 4
NMR data for [SnMe$_2$(phen)L$_2$]

^{1}H	SnCH$_3$	1.37s(6H, ^2J(SnCH) = 80.2 Hz)
	L	7.81m(4H,ortho); 7.63m(6H,meta + para)
	phen	9.47dd(2H,H^{2,9}); 8.35dd(2H,H^{4,7}); 7.87s(2H,H^{5,6}); 7.74dd(2H,H^{3,8})
^{13}C	SnCH$_3$	11.25
	L	156.93(C^5); 134.45(C$_i$); 129.40(C$_m$); 128.91(C$_p$); 123.42(C$_0$)
	phen	150.36(C^2); 136.82(C^4); 144.80(C^{4b}); 129.41(C^5); 126.72(C^{4a}); 123.64(C^3)
^{119}Sn	SnCH$_3$	−77.0 ($W_{1/2}$ = 3000 Hz)
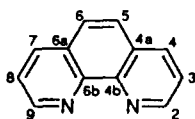
(2) Thioamide bands I and II, present in HL [12] at 1593(m) and 1211(s) cm^{-1} respectively, appear as a medium-strong band at 1223 cm^{-1} and contribute to the band at 1593 cm^{-1} in which phen also participates. Thioamide bands III and IV present in HL at 1051(s) cm^{-1} and 785(w) cm^{-1} shift to 1041(m) cm^{-1} (with a reduction in intensity) and to 770(sh) cm^{-1}. In general, these features resemble those of [SnPh$_3$(L)] and since X-ray analysis showed [SnPh$_3$(L)] to have an *S,N*-coordination [2c], they are in keeping with *S,N*-coordination of L in [SnMe$_2$(phen)L$_2$].

(3) There are no additional bands attributable exclusively to *N*-coordinated L, although L ring vibrations may contribute to the phen and methyl bands at 1082 and 800 cm^{-1}. The fact that several bands may overlap with those of coordinated phen is not surprising, because ring vibrations in this range have previously been found for *N*-coordinated 1-substituted tetrazoles [13,14]. Unfortunately, it hinders IR analysis in this case.

With respect to the organometallic fragment SnC$_2$, a medium band at 557 cm^{-1} is attributed to ν_{asym}(Sn–C), and ν_{sym}(Sn–C) reinforces a ligand band at 510 cm^{-1}.

3.3. NMR study

The NMR data of the title compound are listed in Table 4. In the ^{1}H spectrum the signals assigned to L are deshielded, and the SnCH$_3$ signal is shielded, with respect to the compound [SnMe$_2$(L)$_2$] [2b]. The value of ^2J is larger than in [SnMe$_2$(L)$_2$] but is in the range observed for hexacoordinated compounds [15]. However, the C–Sn–C angle of 134° calculated using this value of ^2J in the Lockhart–Manders relationship [16] is very different from that observed in the solid state.

The appearance of only one set of signals in the proton spectrum of the phen group indicates either a symmetrical environment around the phen or a rapid dynamic motion which may average the signals [17].

The presence of only one peak for C(5) in the ^{13}C spectrum of the complex means that the two coordination modes found in the solid state cannot be distinguished in solution. The position of this signal, deshielded with respect to other essentially *S*-bound compounds and more shielded [2b,2c] than in the free

HL [2c] may indicate an equilibrium between the *S*- and *N*-coordinated forms. The ^{13}C data of the phen group (which likewise feature only one set of signals) confirm the NMR equivalence of the nitrogen atoms of phen.

The ^{119}Sn NMR signal of [SnMe$_2$(phen)L$_2$] is shifted significantly upfield with respect to that of [SnMe$_2$(L)$_2$] [2b]. This is possibly attributable to the phen nitrogen atoms having a greater shielding effect than sulfur, rather than to the coordination number being higher than the six [18] found in the solid state.

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