Comparative Structural Study of Dimethyl(pyridine-2-thiolato)thallium(III) and Dimethylbis(pyridine-2-thiolato)tin(IV)†

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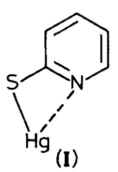
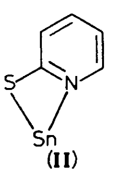
The crystal structures of the [$TlMe_2L$] and [$SnMe_2L_2$] (L = pyridine-2-thiolate) have been determined. Dimethyl(pyridine-2-thiolato)thallium(III) crystallizes in the monoclinic space group $P2_1/n$ (no 14) with a = 8.169(1), b = 13.214(1), c = 8.876(2) Å, β = 104.61(1)°, and Z = 4. Refinement converged to R = 0.047 for 1 531 independent observed reflections. The thallium atom co-ordinates to the two methyl carbons [Tl–C 2.159(8) and 2.199(8) Å], to the pyridine nitrogen [Tl–N 2.494(7) Å], and to two sulphur atoms [Tl–S 3.160(3) and 2.870(2) Å]. Dimethylbis(pyridine-2-thiolato)tin(IV) crystallizes in the monoclinic space group $P2_1/m$ (no 11) with a = 6.664(5), b = 17.342(5), c = 6.943(3) Å, β = 112.53(5)°, and Z = 2. Refinement converged to R = 0.038 for 1 105 independent observed reflections. The tin atom co-ordinates to the two methyl carbons [Sn–C 2.133(9) Å], the two pyridine nitrogens [Sn–N 2.702(5) Å], and the two sulphur atoms [Sn–S 2.487(2) Å]. The structural characteristics of the free ligand are compared with those of the co-ordination compounds, and the mass and ^{13}C n.m.r. spectra of the two complexes are compared.

Concern regarding the environmental and toxicological effects of the biomethylation of heavy metals[1] has led to an increase in research on the co-ordination chemistry of methylmetal species. The cations $TlMe_2^+$ and $SnMe_2^{2+}$, both of which can result from biomethylation,[1] differ in charge but their metal atoms both have formally the same number of electrons in their valency shells; both these methylated cations are stable, and they have similar C–M–C stereochemistry in water.[2] Unlike other organometallic compounds generated by biological systems, they appear to be less toxic than other chemical forms of their metals[3,4] and much less toxic than $HgMe^+$. The possibility that these peculiarities may depend on their co-ordination properties has prompted us to study the co-ordination of these cations with ligands offering a variety of forms of bonding.

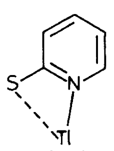
One of the ligands we have considered is 2-mercaptopyridine (HL) which though relatively simple is capable of a number of modes of co-ordination,[5,6] and whose co-ordination to methylmercury(II) we have previously studied.[7] We now report the characteristics of its complexes with dimethylthallium(III) and dimethyltin(IV). We found that in the complexes all the three metals have significantly different environments and L adopts three different co-ordination modes, (I)—(III).



(I)



(II)



(III)

Experimental

Synthesis.—The complex [$TlMe_2L$] (**1**) was prepared as previously.[8] Recrystallization from methanol produced crystals suitable for *X*-ray measurements. The complex [$SnMe_2L_2$] (**2**) was prepared using a method described elsewhere.[9] Sodium hydroxide was added to a solution of the ligand in ethanol, and a solution of [$SnMe_2Cl_2$] in the same solvent then added. After the white solid initially formed had been filtered off, the filtrate afforded crystals suitable for *X*-ray measurements.

X-Ray Data collection and Structure Refinement.—All *X*-ray crystallographic measurements were carried out using a CAD-4 Enraf-Nonius diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. Crystal data and experimental conditions are listed in Table 1. Both structures were solved by Patterson and subsequent Fourier difference maps. The hydrogen atoms of complex (**1**) were not located, but those of (**2**) (except the H atoms of the methyl groups) were located and refined.

A secondary extinction correction[10] was not required for (**1**) but was applied for (**2**) [coefficient: 3.9 721(1) × 10^{-7}]. The atomic scattering factors were taken from Refs. 11 (**1**) and 12 (**2**). Calculations were performed on a DEC Micro VAXII with the programs SHELX 76[13] and VAXSDP[14] for (**1**) and VAXSDP[14] for (**2**). The final atomic co-ordinates for complexes (**1**) and (**2**) are in Tables 2 and 3 respectively, bond distances and angles in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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† *Supplementary data available:* further details have been deposited as supplementary publications CSD-53671 (**1**) and CSD-53209 (**2**), copies of which may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen. Germany.

Table 1. Crystal data and experimental conditions for complexes (**1**) and (**2**)

Compound	(**1**)	(**2**)
Formula	$C_7H_{10}NSTl$	$C_{12}H_{14}N_2S_2Sn$
M	344.60	369.08
System	Monoclinic	Monoclinic
a/Å	8.169(1)	6.664(5)
b/Å	13.214(1)	17.342(5)
c/Å	8.876(2)	6.943(3)
β/°	104.61(1)	112.53(5)
U/Å^3	927.08	740.7
Space group	$P2_1/n$ (no. 14)	$P2_1/m$ (no. 11)
Z	4	2
D_c/g cm^{-3}	2.469	1.655
Scan technique	ω—2θ	ω—θ
μ/cm^{-1}	177.51	19.83
F(000)	624	364
Crystal dimensions/mm	0.250 × 0.125 × 0.047	0.50 × 0.20 × 0.15
Absorption correction	Analytical	DIFABS*
Minimum, maximum absorption corrections	0.200, 2.030	0.641, 1.382
Range *h,k,l*	−10 to 10, −1 to 16, 0 to 11	0 to 7, 0 to 20, −8 to 8
Standard reflections	0, $\bar{12}$, 0	3, $\bar{6}$, 0; 1, $\bar{7}$, $\bar{2}$
Reflections measured	2 448	2 932
θ range/°	1—27	3—25
Unique reflections and R_{int}	1 894, 0.044	2 299, 0.025
Reflections with $I > 3\sigma(I)$	1 531	1 105
Weighting scheme	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
Parameters refined	91	83
R	0.047	0.038
R'	0.047	0.044
Max. shift/e.s.d.	0.01	0.001
Max. height in final ΔF map/ e Å^{-3}	2.45	0.855
Error in an observation of unit weight	6.33	1.345

* N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

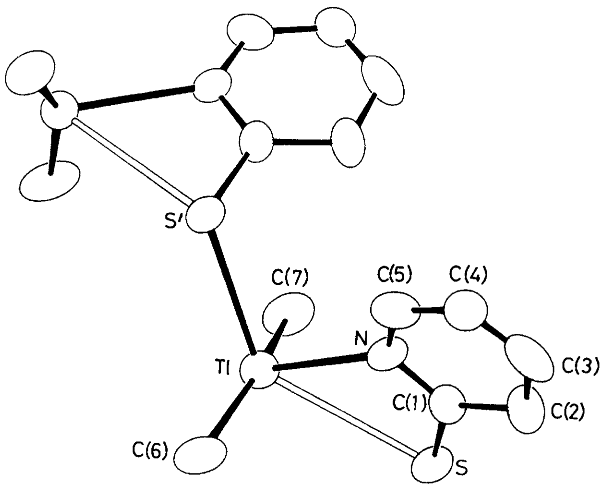


Figure 1. The molecular structure of [$TlMe_2L$] (**1**), with the atom numbering scheme

Mass and ^{13}C *N.M.R. spectra.*—Mass spectra were recorded in a Kratos MS50TC spectrometer connected to a DS 90 data system, using electron impact (70 eV, *ca.* 1.12 × 10^{-17} J) with the source at 250 °C and operating at an acceleration voltage of 8 kV. The samples were introduced *via* a direct injection probe, which was heated to 400 °C. Carbon-13 n.m.r. spectra were recorded in $(CD_3)_2SO$ solutions on a Bruker WM250 instrument.

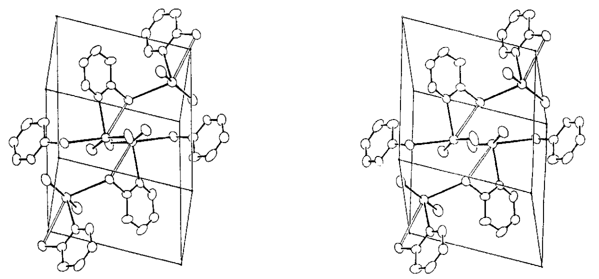


Figure 2. Stereoscopic view of the molecular packing in compound (**1**)

Results and Discussion

Description of the Structure of Complex (**1**).—In the determination of the structure of complex (**1**), scattering was heavily dominated by the Tl atom, the effect of which on final fractional co-ordinates and calculated bond lengths and angles has been discussed previously.[15] The final difference map shows fluctuations of about ± 2.5 e Å^{-3}, all of them about 1 Å from the thallium atom, a plausible explanation for which has been suggested elsewhere.[15]

Figure 1 shows the atom numbering scheme used and Figure 2 a stereoscopic view of the unit cell. The thallium atom is co-ordinated to the two methyl groups, the N atom of one ligand molecule and the S atom of another ligand molecule in the position $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$. A weaker interaction between the thallium atom and the sulphur atom of the first ligand molecule results in the ligand providing an asymmetric sulphur bridge between two metal centres. If the weak Tl $\cdots$ S interaction is included, the co-ordination number of Tl in [$TlMe_2L$] is thus

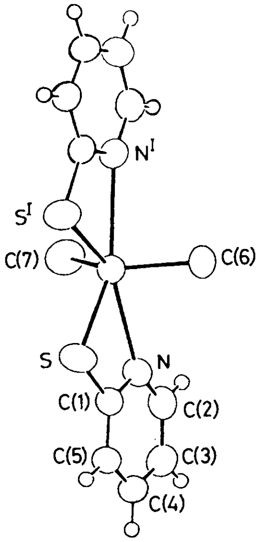


Figure 3. The molecular structure of [$SnMe_2L_2$] (**2**), with the atom numbering scheme

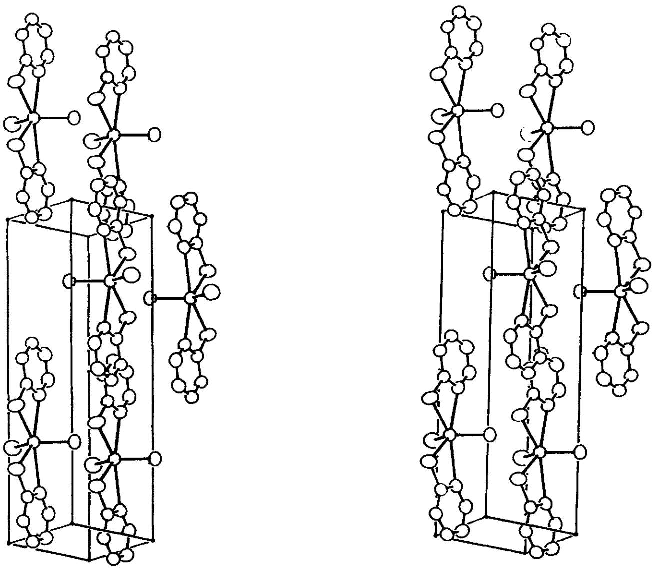


Figure 4. Stereoscopic view of the molecular packing in compound (**2**)

Table 2. Positional parameters and their estimated standard deviations (e.s.d.s) for complex (**1**)

Atom	*x*	*y*	*z*
Tl	0.379 90(8)	0.260 02(4)	0.363 13(7)
S	0.560 7(5)	0.327 3(3)	0.706 4(5)
N	0.321(2)	0.191(1)	0.606(1)
C(1)	0.422(2)	0.233(1)	0.730(2)
C(2)	0.417(2)	0.198(1)	0.885(2)
C(3)	0.301(2)	0.117(2)	0.888(2)
C(4)	0.206(2)	0.075(1)	0.759(2)
C(5)	0.221(2)	0.113(1)	0.621(2)
C(6)	0.286(2)	0.413(1)	0.337(2)
C(7)	0.542(2)	0.131(1)	0.343(2)

Table 3. Positional parameters and their e.s.d.s for complex (**2**)

Atom	*x*	*y*	*z*
Sn	0.289 6(1)	0.250	0.240 5(1)
S	0.539 8(3)	0.348 6(1)	0.197 1(3)
N	0.199 9(8)	0.401 2(3)	0.257 5(8)
C(1)	0.381(1)	0.424 2(4)	0.227 9(9)
C(2)	0.070(1)	0.456 3(4)	0.281(1)
C(3)	0.109(1)	0.533 3(4)	0.276(1)
C(4)	0.295(1)	0.556 2(4)	0.247(1)
C(5)	0.432(1)	0.501 4(4)	0.223(1)
C(6)	−0.004(2)	0.250	−0.031(2)
C(7)	0.307(2)	0.250	0.553(2)

Table 4. Bond lengths (Å) and angles (°) with e.s.d.s for complex (**1**)

Tl–S	3.160(3)	N–C(1)	1.33(1)
Tl–S′*	2.870(2)	N–C(5)	1.34(2)
Tl–N	2.494(7)	C(1)–C(2)	1.46(2)
Tl–C(6)	2.159(8)	C(2)–C(3)	1.44(1)
Tl–C(7)	2.199(8)	C(3)–C(4)	1.33(1)
S–C(1)	1.730(8)	C(4)–C(5)	1.36(1)
S–Tl–S′	136.65(9)	C(6)–Tl–C(7)	158.0(4)
S–Tl–N	54.2(2)	C(1)–N–C(5)	120.3(7)
S–Tl–C(6)	84.7(3)	S–C(1)–N	119.5(6)
S–Tl–C(7)	98.7(3)	S–C(1)–C(2)	120.8(7)
S′–Tl–N	85.5(2)	N–C(1)–C(2)	119.6(8)
S′–Tl–C(6)	94.1(3)	C(1)–C(2)–C(3)	115.3(9)
S′–Tl–C(7)	98.1(3)	C(2)–C(3)–C(4)	123.0(9)
N–Tl–C(6)	107.2(3)	C(3)–C(4)–C(5)	116.7(8)
N–Tl–C(7)	92.2(3)	N–C(5)–C(4)	125.0(9)

* Symmetry code: $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Table 5. Bond lengths (Å) and angles (°) with e.s.d.s for complex (**2**)

Sn–S	2.487(2)	C(2)–C(3)	1.36(2)
Sn–N	2.702(5)	C(3)–C(4)	1.38(1)
Sn–C(6)	2.133(9)	C(4)–C(5)	1.38(2)
Sn–C(7)	2.13(1)	C(2)–H(2)	0.977(8)
S–C(1)	1.751(7)	C(3)–H(3)	0.979(8)
N–C(1)	1.36(1)	C(4)–H(4)	0.967(7)
N–C(2)	1.34(1)	C(5)–H(5)	0.972(8)
C(1)–C(5)	1.386(9)		
S–Sn–S^{I}*	86.91(7)	C(1)–N–C(2)	117.4(6)
S–Sn–N	60.5(1)	S–C(1)–N	114.4(5)
S–Sn–N^{I}	147.4(1)	S–C(1)–C(5)	123.4(6)
S–Sn–C(6)	108.8(3)	N–C(1)–C(5)	122.2(6)
S–Sn–C(7)	110.3(2)	N–C(2)–C(3)	123.8(7)
N–Sn–N^{I}	152.1(2)	C(2)–C(3)–C(4)	118.4(7)
N–Sn–C(6)	84.0(1)	C(3)–C(4)–C(5)	119.6(6)
N–Sn–C(7)	83.2(1)	C(1)–C(5)–C(4)	118.7(7)
C(6)–Sn–C(7)	125.1(5)		

* Symmetry code: I $x, \frac{1}{2} - y, z$.

five. The co-ordination polyhedron may be described as a deformed octahedron with one vacant position.

The $TlMe_2^+$ derivatives whose structures have been determined by *X*-ray diffraction may be divided in two groups: (*a*) halides or pseudohalides[16,17] and (*b*) complexes with organic ligands. The latter may in turn be classified according to whether the donor atom or atoms are O,[18–23] N,[24–26] S,[19] N and O,[27] O and S,[8,28] N and S,[29,30] or O, N, and S.[15–31] Interaction with the anions ClO_4^- or NO_3^- was also detected in some of these complexes.[24–26] If weak interactions are also taken into account, the ranges of Tl–L bond lengths observed hitherto are 2.36—3.25 Å for Tl–O, 2.55—3.13 A, for Tl–N, and 2.63—3.35 Å for Tl–S.

The Tl–N distance observed in [$TlMe_2L$] in the present study, 2.494 Å, is shorter than any such distance reported previously, showing it to be a very strong bond. The Tl–S bond length, 2.870 Å, is within the normal range for polydentate

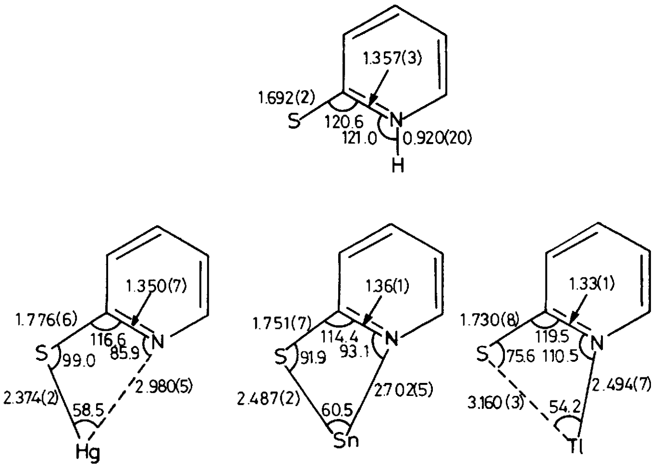


Figure 5. Details (lengths in Å, angles in °) of the structures of complexes (**1**), (**2**), [HgMeL], and HL

ligands, while the other Tl–S distance, 3.160 Å, though shorter than the sum of the van der Waals radii (3.76 Å[32]), indicates a weak interaction. The two Tl–C bonds are of normal length; the bending of the C–Tl–C unit to reduce steric interactions is a good deal less than in (2,3-dihydro-2-thioxo-1*H*-pyrimidin-4-unato)dimethylthallium(III).[15] The ligand is very nearly planar.

Description of the Structure of Complex (**2**).—The atom numbering scheme for [$SnMe_2L_2$] is shown in Figure 3 and a stereoscopic view of its unit cell in Figure 4. The crystal consists of monomer units in which Sn is co-ordinated to two methyl groups and to the sulphur and nitrogen atoms of two ligand molecules. The Sn–C distance, 2.133(9) Å, is similar to that found in other [SnR_2(chelate)$_2$] systems,[33] and the Sn–S distance, 2.487(2) Å, is close to the typical length of a single covalent bond.[34,35] The Sn–N distance, though less than the sum of the van der Waals radii,[32] is one of the largest reported for organotin compounds, though longer bonds have been reported in other tin species.[36–40]

The above co-ordination scheme is practically identical to that found in di-n-butylbis(5-nitropyridine-2-thiolato)tin(IV) by Domazetis *et al.*[36] who described it as a distorted octahedron, though Ng *et al.*[33] consider that the co-ordination polyhedra of this and similar compounds are best described as skew trapezoidal bipyramids.

On the other hand, the environment of Sn in complex (**2**) is also comparable to that found in [$SnMe_2(O_2CMe)_2$] and [$SnMe_2(O_2CC_6H_4NH_2$-*p*)$_2$],[41,42] in which it was described as a bicapped tetrahedron; though there are significant differences due to the structural differences between the ligands (particularly the fact that 2-mercaptopyridine co-ordinates *via* two different atoms forming an asymmetrical SCN unit, whereas the other two complexes involve co-ordination *via* just the oxygen atoms of symmetrical carboxylate groups), there is also marked similarity in that among the four atoms defining the tetrahedron in (**2**) [C(6), C(7), S, and S^I] there are four 'normal' tetrahedral angles [108.8(3)—110.3(2)°] and two (C–Sn–C and S–Sn–S) that are deformed by the influence of the capping atoms. The co-ordination polyhedron of Sn in (**2**) may therefore be correctly described either as a skew trapezoidal bipyramid or as a bicapped tetrahedron.

Both the ligand molecules in complex (**2**) are planar and both lie, with Sn, in the same best least-squares plane, with no significant deviations. This complex thus differs strikingly from dichlorobis(pyridine-2-thiolato)tin(IV),[43] in which the planes of the two ligand molecules, which like L are bidentate, lie at 90° to each other.

Table 6. Mass spectra of complexes (**1**) and (**2**)

Complex (1)			Complex (2)		
Ion	m/z*	Abundance	Ion	m/z*	Abundance
[M_2−Me]$^+$	675	1.2	[M + HL]$^+$	481	0.2
[M + Tl]$^+$	550	0.1	[M − Me]$^+$	355	18.4
[TlLTl]$^+$	520	0.1	[M − L]$^+$	260	34.2
M^+	345	1.1			
[M − Me]$^+$	330	19.7	[M − L − 2Me]$^+$	230	43.8
[M − 2Me]$^+$	315	11.6	[HL]$^+$	111	48.8
[$TlMe_2$]$^+$	235	11.1	[C_5H_5N − H]$^+$	78	100.0
[TlMe]$^+$	220	9.4			
Tl$^+$	205	100.0	—	69	18.1
[HL]$^+$	111	2.3			
[C_5H_5N − H]$^+$	78	2.9			

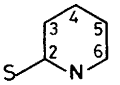
* Nominal values calculated using the most abundant isotope ^{120}Sn or ^{205}Tl.

Although the structure of complex (**1**) is formed by chains while those of (**2**) and [HgMeL][7] contain isolated molecules, it is interesting to analyze the local changes in the molecular fragment M–N–C(1)–S when the three complexes are considered together with the relevant region of the free ligand molecule[44] (Figure 5). According to the bond distances the N–M bond is strong in (**1**), weak in [HgMeL], and intermediate in (**2**), and as the bond weakens the metal atom moves away from the direction in which the donor pair's charge density is greatest, with the result that the angle C(1)–N–M narrows; at the same time the S–M bond becomes stronger and the angle C(1)–S–M widens. Note that the distance C(1)–S varies considerably among the three complexes, increasing as the distance S–M decreases; in (**1**), though not so short as in the free ligand, it must have a considerable degree of double-bond nature, while in [HgMeL] it is close to the theoretical length of a single C–S bond, 1.81 Å.[45] These trends mean that the three organometallic cations may be ranked in the order $TlMe_2^+ < SnMe_2^{2+} < HgMe^+$ as regards their ability to transform the ligand from its thione to its thiol form, which suggests that the 'softnesses'[46] of the three cations increase in the same order.

Mass Spectra.—Table 6 lists mass spectral data for complexes (**1**) and (**2**). The mass spectra of dimethylthallium(III) compounds have hitherto received little attention.[47] The stability of the complex(**1**) allows the appearance of the molecular ion M^+. There appear to be at least two effective primary ionization processes, one involving the breaking of the metal–ligand bond and the other demethylation of Tl. The presence of an intense signal for $TlMe_2$ is not surprising in view of the known stability of this ion. The region of the spectrum corresponding to ions with greater mass than M^+ varies with the experimental conditions, especially the heating rate and sample-injection temperature; the species listed in Table 6 were detected with slow heating of the probe from room temperature to *ca.* 150 °C. Though the nature and abundance of the high m/z species is variable, the presence of bimetallic ions is in keeping with the associated nature of the solid.

The molecular ion of complex (**2**) was not detected. The loss of a deprotonated ligand molecule appears to be a more frequent primary ionization process than the loss of a methyl group, though as in electron-impact studies of [$SnMe_2Cl_2(HL)_2$][48] the most abundant metal-bearing ion is SnL. For both these complexes, the fragment [HL]$^+$ accounts for a large proportion of the ion current. Very weak peaks whose isotopic profile corresponds to [M + HL]$^+$ (0.2%) and [M + (M + H)]$^+$ (0.1%) were also observed. This species can be generated by ion-neutral molecule reactions.

Table 7. Carbon-13 n.m.r. spectroscopic data (p.p.m. from $SiMe_4$)[a]



	C(2)	$\Delta\delta^a$	C(3)	$\Delta\delta$	C(4)	$\Delta\delta$	C(5)	$\Delta\delta$	C(6)	$\Delta\delta$	CH_3
HL	177.7	—	133.1	—	137.4	—	112.9	—	137.8	—	—
$[TlMe_2L]$	175.2	2.5	129.7	3.4	136.0	1.4	116.4	−3.5	147.0	−9.2	22.6
$[SnMe_2L_2]$	160.0	17.7	124.2	8.9	137.9	−0.5	118.5	−5.6	146.0	−9.1	7.6
L'^b	160.4	17.3	121.8	11.3	136.5	0.9	119.7	−6.8	150.0	−12.2	12.9

[a] $\Delta\delta = \delta(HL) - \delta(MR_nL_m$ or $L')$. [b] In $(CD_3)_2CO$.

^{13}C *N.M.R. Spectra.*—Table 7 lists the chief features of the ^{13}C n.m.r. spectra of the ligand,[49] its S-methylated derivative L′,[50] and its complexes with dimethylthallium(III)[8] and dimethyltin(IV).

The signals of carbons C(2), C(3), C(5), and C(6) show important shifts on going from HL (thione form) to L′ (thiol form). The position of these signals for complexes (**1**) and (**2**) are, in general, in keeping with the fact that, also in solution, the ligand in the tin complex has a higher thiol character than in the thallium complex because the spectrum of (**1**) is more closely related with the spectrum of the S-methylated ligand.

Acknowledgements

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