Dimethylthallium(III) and Methylmercury(II) Derivatives of Pyridine-2-carbaldehyde Thiosemicarbazone: Synthesis and Structure†

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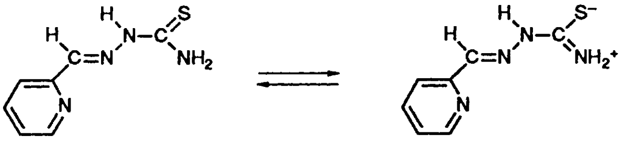
The reaction of dimethylthallium(III) hydroxide and methylmercury(II) chloride with pyridine-2-carbaldehyde thiosemicarbazone (HL) and its sodium salt, respectively, afforded [$TlMe_2$(L)] and [HgMe(L)]. The thallium complex crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with $a = 11.005(2)$, $b = 12.153(2)$, $c = 10.822(1)$ Å, $\alpha = 110.18(1)$, $\beta = 99.79(1)$, $\gamma = 70.39(1)°$, and $Z = 4$ ($R = 0.031$, $R' = 0.035$). The unit cell has two independent molecules in each asymmetric unit, both containing an N,N′,S-tridentate ligand but with significant differences in bond distances and angles. The ^1H NMR spectrum of [$TlMe_2$(L)] in $CDCl_3$ indicates that the bonding scheme observed in the solid state is retained in solution. Infrared data for [HgMe(L)] in the solid state suggest that the metal is N(hydrazinic), S-co-ordinated; in solution in chloroform, [HgMe(L)] consists of a mixture of (*E*) and (*Z*) isomers.

The structural chemistry of diorganothallium(III) compounds is characterized by two main features: (*i*) the C–Tl–C unit is usually (although not always[1]) almost linear; and (*ii*) the co-ordination number of the metal is four or more. Even with monodentate ligands,[2] bridging bonds giving dimeric molecules increase the number of atoms around the metal to four, while with bidentate ligands intermolecular interactions lead, with few known exceptions,[3] to co-ordination numbers greater than four.

Although there is a certain amount of structural information available concerning dimethylthallium(III) complexes with ligands of high denticity,[4] only one compound with a tridentate ligand has been studied by X-ray diffraction.[5] In this cationic complex the presence of an anion and a water molecule lead to a seven-co-ordinate thallium atom, weak interactions included. As far as we know, no neutral compounds with tridentate ligands have been studied. To see what can happen in the neutral case, we have now studied the interaction of the dimethylthallium(III) cation with the usually N,N′,S-dentate[6] ligand pyridine-2-carbaldehyde thiosemicarbazone (HL), which once deprotonated gives a monocharged anion able to form a neutral complex with $TlMe_2^+$.



It has recently been observed[7] that N,S-dentate thiosemicarbazones co-ordinate rather similarly to methylmercury(II) and dimethylthallium(III), the mercury complexes having co-ordination numbers greater than the usual two. Although the spectroscopic evidence indicates that L is not co-ordinated through its heterocyclic ring in [HgMe(L)], studies in solution in Me_2SO show the presence of more than one species. This paper suggests an explanation of this fact, and reports the structural characteristics of the [$TlMe_2$(L)] and [HgMe(L)] complexes.

Experimental

Thiosemicarbazide (Merck), pyridine-2-carbaldehyde (Merck) and methylmercury(II) chloride (Ventron) were used as received. The compound HL and dimethylthallium(III) hydroxide were prepared as before.[6,7b] Analytical data were obtained from Galbraith Lab. Inc., Knoxville, TN or using a Perkin Elmer model 240B analyser. Melting points were determined in a Büchi apparatus. Infrared spectra were recorded using Nujol mulls or KBr discs in a Perkin Elmer 180 spectrometer, ^1H spectra on a Bruker WM-250 apparatus. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS-90 data system and operating in electron impact(EI) mode (direct insertion probe, 70 eV, 250 °C) or FAB (*m*-nitrobenzyl alcohol, Xe, 8 eV) conditions. All the fragments were identified using DS-90 software.

Synthesis of [HgMe(L)].—The compound [HgMe(Cl)] (1.5 g, 6.0 mmol) dissolved in dichloromethane (50 cm^3) was added to an aqueous solution (50 cm^3) of the sodium salt of the ligand (1.08 g, 6.0 mmol) prepared by reaction between equimolar quantities of HL and aqueous NaOH. The two phases were stirred for 4 h and the organic layer was then decanted off and cooled until a green solid formed which was isolated and dried under vacuum, m.p. 130 °C (Found: C, 24.9; H, 2.8; N, 14.2. $C_8H_{10}HgN_4S$ requires C, 24.3; H, 2.6; N, 14.2%). The main metallated ions in the EI mass spectrum were at m/z (%) = 464 (Me_2Hg_2S, 28), 449 ($MeHg_2S$, 16), 434 (Hg_2S, 5), 417 ($MeHg_2$, 3), 402 (Hg_2, 6), 381 (M − Me, 30), 249 (MeHgS, 16), 232 (Me_2Hg, 9), 217 (MeHg, 24), 202 (Hg, 18), and base peak 92 (C_6H_6N, 100).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

Table 1 Positional parameters for [TlMe$_2$(L)], with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Tl(1)	0.142 60(4)	0.353 79(4)	0.062 65(5)
Tl(2)	0.124 78(5)	0.797 16(4)	0.489 79(5)
S(1)	0.163 4(3)	0.595 9(3)	0.137 9(3)
S(2)	0.072 7(4)	1.033 3(3)	0.673 3(3)
N(1)	0.360(1)	0.640 1(8)	0.076(1)
N(2)	0.414 5(9)	0.448 9(8)	0.090 0(9)
N(3)	0.376 0(8)	0.360 7(8)	0.111 8(9)
N(4)	0.319(1)	0.161 1(9)	0.122(1)
N(11)	−0.023(1)	1.108 8(9)	0.904(1)
N(12)	0.090(1)	0.905 5(8)	0.843 6(9)
N(13)	0.156 0(8)	0.807 7(8)	0.747 1(8)
N(14)	0.276(1)	0.598(1)	0.558(1)
C(1)	0.323(1)	0.553(1)	0.100(1)
C(2)	0.466(1)	0.269(1)	0.127(1)
C(3)	0.441(1)	0.164(1)	0.146(1)
C(4)	0.538(1)	0.077(1)	0.189(1)
C(5)	0.511(2)	−0.015(1)	0.211(2)
C(6)	0.385(2)	−0.017(1)	0.193(2)
C(7)	0.291(1)	0.070(1)	0.145(1)
C(8)	0.179(1)	0.307(1)	−0.138(1)
C(9)	0.064(1)	0.387(1)	0.242(1)
C(11)	0.046(1)	1.009(1)	0.813(1)
C(12)	0.203(1)	0.708 1(9)	0.775(1)
C(13)	0.267(1)	0.594 8(9)	0.678(1)
C(14)	0.315(1)	0.488(1)	0.712(1)
C(15)	0.372(2)	0.378(1)	0.618(1)
C(16)	0.380(2)	0.381(1)	0.495(2)
C(17)	0.333(2)	0.493(1)	0.470(1)
C(18)	−0.044(1)	0.752(1)	0.494(1)
C(19)	0.290(1)	0.821(1)	0.437(2)

Table 2 Bond distances (Å) for [TlMe$_2$(L)]

Molecule 1		Molecule 2	
Tl(1)–S(1)	2.848(3)	Tl(2)–S(2)	2.803(2)
Tl(1)–S(1$^{\mathrm{I}}$)	3.671(2)	Tl(2)–S(2$^{\mathrm{II}}$)	3.207(3)
Tl(1)–N(3)	2.557(5)	Tl(2)–N(13)	2.712(5)
Tl(1)–N(4)	2.686(8)	Tl(2)–N(14)	2.700(6)
Tl(1)–C(8)	2.115(8)	Tl(2)–C(18)	2.125(9)
Tl(1)–C(9)	2.12(1)	Tl(2)–C(19)	2.13(1)
S(1)–C(1)	1.738(8)	S(2)–C(11)	1.719(7)
N(1)–C(1)	1.368(9)	N(11)–C(11)	1.351(9)
N(2)–N(3)	1.378(8)	N(12)–N(13)	1.363(8)
N(2)–C(1)	1.30(1)	N(12)–C(11)	1.331(9)
N(3)–C(2)	1.259(8)	N(13)–C(12)	1.267(8)
N(4)–C(3)	1.35(1)	N(14)–C(13)	1.339(9)
N(4)–C(7)	1.34(1)	N(14)–C(17)	1.33(2)
C(2)–C(3)	1.47(2)	C(12)–C(13)	1.447(9)
C(3)–C(4)	1.37(2)	C(13)–C(14)	1.38(2)
C(4)–C(5)	1.36(1)	C(14)–C(15)	1.39(1)
C(5)–C(6)	1.38(2)	C(15)–C(16)	1.36(1)
C(6)–C(7)	1.38(1)	C(16)–C(17)	1.38(1)
N(1) $\cdots$ N(2$^{\mathrm{III}}$)	2.990(9)	N(11) $\cdots$ N(12$^{\mathrm{IV}}$)	3.022(8)

Symmetry codes: I $-x, -y + 1, -z$; II $x, -y + 2, -z + 1$; III $-x + 1, -y + 1, -z$; IV $-x, -y + 2, -z + 2$.

Table 3 Bond angles (°) for [TlMe$_2$(L)]

Molecule 1		Molecule 2	
S(1)–Tl(1)–S(1$^{\mathrm{I}}$)	97.91(6)	S(2)–Tl(2)–S(2$^{\mathrm{II}}$)	76.73(6)
S(1)–Tl(1)–N(3)	66.8(1)	S(2)–Tl(2)–N(13)	64.1(1)
S(1)–Tl(1)–N(4)	125.9(2)	S(2)–Tl(2)–N(14)	121.3(1)
S(1)–Tl(1)–C(8)	95.7(2)	S(2)–Tl(2)–C(18)	101.1(3)
S(1)–Tl(1)–C(9)	92.8(3)	S(2)–Tl(2)–C(19)	89.5(3)
S(1$^{\mathrm{I}}$)–Tl(1)–N(3)	149.9(1)	S(2$^{\mathrm{II}}$)–Tl(2)–N(13)	133.9(1)
S(1$^{\mathrm{I}}$)–Tl(1)–N(4)	136.1(2)	S(2$^{\mathrm{II}}$)–Tl(2)–N(14)	161.7(2)
S(1$^{\mathrm{I}}$)–Tl(1)–C(8)	70.0(3)	S(2$^{\mathrm{II}}$)–Tl(2)–C(18)	81.4(2)
S(1$^{\mathrm{I}}$)–Tl(1)–C(9)	97.4(3)	S(2$^{\mathrm{II}}$)–Tl(2)–C(19)	93.3(3)
N(3)–Tl(1)–N(4)	63.1(2)	N(13)–Tl(2)–N(14)	60.8(2)
N(3)–Tl(1)–C(8)	85.4(2)	N(13)–Tl(2)–C(18)	83.1(3)
N(3)–Tl(1)–C(9)	108.7(3)	N(13)–Tl(2)–C(19)	109.2(3)
N(4)–Tl(1)–C(8)	99.3(3)	N(14)–Tl(2)–C(18)	91.2(3)
N(4)–Tl(1)–C(9)	85.0(3)	N(14)–Tl(2)–C(19)	90.2(3)
C(8)–Tl(1)–C(9)	165.7(3)	C(18)–Tl(2)–C(19)	166.5(4)
Tl(1)–S(1)–C(1)	96.6(3)	Tl(2)–S(2)–C(11)	102.6(8)
N(3)–N(2)–C(1)	114.1(6)	N(13)–N(12)–C(11)	113.7(6)
Tl(1)–N(3)–N(2)	122.0(4)	Tl(2)–N(13)–N(12)	123.0(4)
N(2)–N(3)–C(2)	115.4(6)	N(12)–N(13)–C(12)	115.3(6)
Tl(1)–N(4)–C(3)	116.8(5)	Tl(2)–N(14)–C(13)	117.8(5)
C(3)–N(4)–C(7)	117.7(8)	C(13)–N(14)–C(17)	117.4(7)
S(1)–C(1)–N(1)	115.5(6)	S(2)–C(11)–N(11)	116.4(5)
S(1)–C(1)–N(2)	129.9(6)	S(2)–C(11)–N(12)	127.5(5)
N(1)–C(1)–N(2)	114.5(7)	N(11)–C(11)–N(12)	116.1(6)
N(3)–C(2)–C(3)	122.2(7)	N(13)–C(12)–C(13)	121.1(6)
N(4)–C(3)–C(2)	116.0(7)	N(14)–C(13)–C(12)	118.3(6)
N(4)–C(3)–C(4)	122.6(8)	N(14)–C(13)–C(14)	122.2(7)
C(2)–C(3)–C(4)	121.5(7)	C(12)–C(13)–C(14)	119.5(7)
C(3)–C(4)–C(5)	120.1(9)	C(13)–C(14)–C(15)	119.6(8)
C(4)–C(5)–C(6)	117.9(9)	C(14)–C(15)–C(16)	118.2(9)
C(5)–C(6)–C(7)	120.0(8)	C(15)–C(16)–C(17)	119.3(8)
N(4)–C(7)–C(6)	121.6(9)	N(14)–C(17)–C(16)	123.5(8)

Synthesis of [TlMe$_2$(L)].—A solution of ligand HL (0.49 g, 2.8 mmol) in hot ethanol (50 cm^3) was slowly added to [TlMe$_2$(OH)] (2.8 mmol). The solution was stirred for 3 d, and the yellow crystalline solid formed was filtered off and dried *in vacuo*, m.p. 170 °C (Found: C, 26.0; H, 3.1; N, 14.0. $C_9H_{13}N_4STl$ requires C, 26.1; H, 3.2; N, 13.5%). The main metallated ions in the FAB mass spectrum (based on the isotope ^{205}Tl) were at *m*/*z* (%) = 415 (*M*, 26), 399 (*M* − Me, 58), 235 (Me$_2$Tl, 100) and 205 (Tl, 87).

Determination of the Crystal Structure of [TlMe$_2$(L)].—*Crystal data.* $C_9H_{13}N_4STl$, $M = 413.66$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.005(2)$, $b = 12.153(2)$, $c = 10.822(1)$ Å, $\alpha = 110.18(1)$, $\beta = 99.79(1)$, $\gamma = 70.39(1)°$, $U = 1277.6$ Å^3, $Z = 4$, $D_c = 2.151$ g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, $\mu = 129.059$ cm^{-1}, $F(000) = 768$. Crystal dimensions: 0.08 × 0.24 × 0.32 mm.

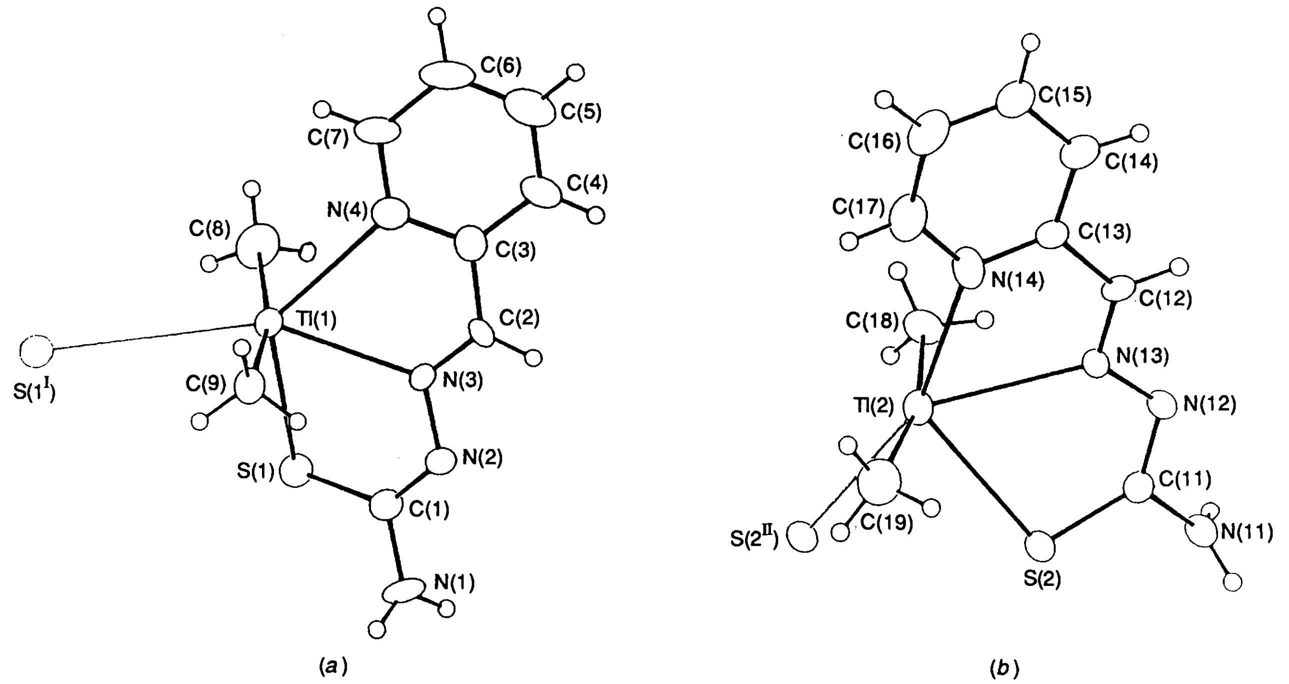
Data collection and processing. Enraf-Nonius CAD-4 diffractometer, ω–θ mode, graphite-monochromated Mo-Kα radiation; 3763 reflections measured ($3 < \theta < 23°, 0 < h < 12, -13 < k < 13, -11 < l < 11$), 3547 unique, giving 2503 with $I > 3\sigma(I)$.

Structure analysis and refinement. Patterson analysis followed by normal Fourier difference techniques enabled all the non-hydrogen atoms in the structure to be located. The H atoms were introduced in calculated positions with fixed C–H distances and isotropic thermal parameters (C–H 0.95 Å, $B_{iso} = 4$ Å^2). In the final cycles of full-matrix least-squares refinement all atoms were treated as anisotropic. The weighting scheme was $w^{-1} = \sigma^2(F_o)$. Absorption corrections were applied at a later stage in the refinement.[8] A final Fourier difference map showed a peak of maximum electron density at 0.762 e Å^{-3}. The programs and computer used, and sources of scattering factor data, are given in ref. 9. Final R and R' values were 0.031 and 0.035. Atomic positions are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal Structure.—Fig. 1 shows the numbering scheme of the two independent molecules (1 and 2) contained in each asymmetric unit, which have similar co-ordination schemes but differ significantly in bond distances and angles (Tables 2 and 3). In both molecules the ligand is tridentate *via* its sulfur, N(3) [or N(13)] and pyridine nitrogen atoms. The co-ordination sphere of the metal is completed by the two methyl groups, which are



(*a*) (*b*)

Fig. 1 An ORTEP drawing of [TlMe$_2$(L)] showing the molecular structure and labelling scheme: (*a*) molecule 1, (*b*) molecule 2 (see text)

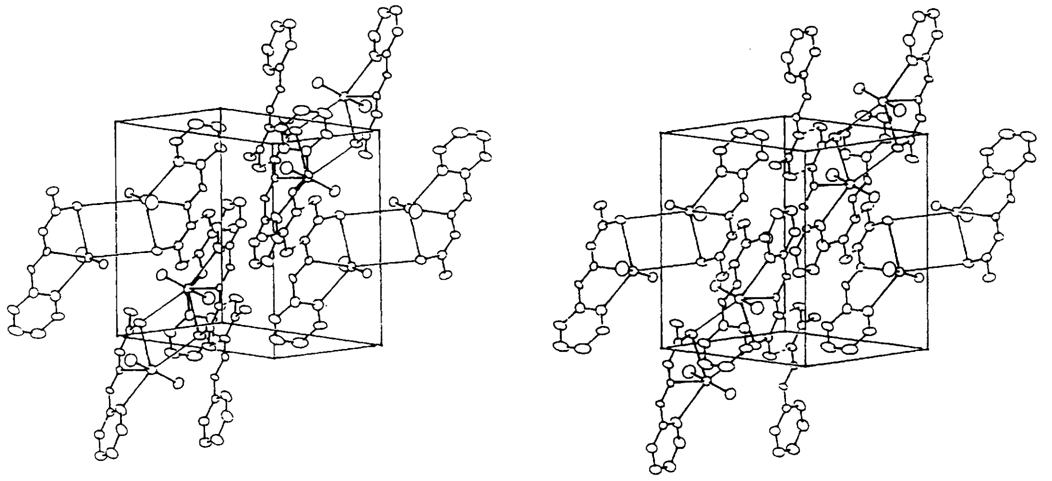
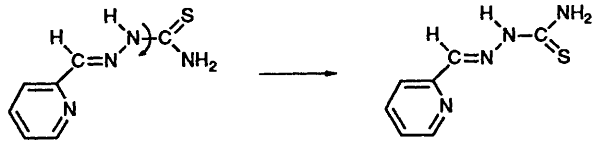


Fig. 2 Stereoscopic view of the molecular packing of [TlMe$_2$(L)]

such that the C–Tl–C unit is nearly linear and the thallium–carbon distances unremarkable. The distance from the thallium atom to the sulfur atom of a neighbour ligand is shorter than the sum of the van der Waals radii (3.76 Å[10]) but nevertheless rather long: in molecule 1 this distance, Tl(1)–S(1$^{\text{I}}$), is 3.671(2) Å, which is larger than in (dithiocarbamato)diphenylthallium(III)[3] the first reported neutral [TlR$_2$(X)] species considered to be non-oligomeric; in molecule 2 the Tl(2)–S(2$^{\text{II}}$) distance is shorter (Table 2), giving rise to weakly bonded dimers (Fig. 2). Other differences between molecules 1 and 2 (Tables 2 and 3) can be summarized as follows: (*i*) in molecule 1 the Tl–N distances are shorter and the intramolecular Tl–S bond longer than in molecule 2; and (*ii*) the ligand is more planar in molecule 2 than in 1 [χ^2 = 43.4 and 325.7 for the respective thiosemicarbazone fragments, with the dihedral angle between this fragment and the pyridine ring being 9(1)° in molecule 2 and 24.9(3)° in 1].

It is as if, in molecule 1, the overall conformational change



normally undergone by the ligand upon co-ordination were frozen by crystallization before total planarity is reached. The intermolecular N(1)···N(2) [or N(11)···N(12)] distances (Table 2, Fig. 2) indicate the presence of hydrogen bonds, as in the dimethylthallium(III) complex of cyclopentanone thiosemicarbazone.[7b]

Table 4 lists bond distances and angles in the ligand and in all its complexes we know of for which they have been determined. For ML$_n$ (L = deprotonated ligand), the significant number of data listed allow more confident discussion of co-ordination-induced changes than in previous papers.[6,11] The changes in

Table 4 Some distances (Å) and angles (°) of pyridine-2-carbaldehyde thiosemicarbazone in the monohydrate of the free ligand and in its complexes (numbering scheme in Fig. 1)

Compound[a]	C(1)–S(1)	C(1)–N(1)	C(1)–N(2)	N(2)–N(3)	N(3)–C(2)	C(2)–C(3)	C(3)–N(4)	N(4)–C(7)	Ref.
HL·H_2O	1.698(3)	1.317(4)	1.358(4)	1.369(3)	1.276(4)	1.457(4)	1.345(4)	1.338(4)	12
$[\{Cu(HL)(SO_4)_2\}_2]$	1.703(3)	1.308(3)	1.362(3)	1.366(3)	1.277(3)	1.457(3)	1.361(3)	1.326(3)	13
$[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$	1.716(3)	1.316(4)	1.342(4)	1.354(4)	1.293(4)	1.463(4)	1.350(4)	1.348(4)	11
$[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$	1.708(3)	1.313(5)	1.346(4)	1.363(4)	1.285(4)	1.459(5)	1.369(4)	1.325(4)	11
$[CdCl_2(HL)]\cdot H_2O$	1.687(4)	1.323(5)	1.356(4)	1.355(4)	1.282(4)	1.461(5)	1.347(4)	1.326(5)	6
$[\{CuL(MeCO_2)\}_2]$	1.725(2)	1.333(4)	1.335(3)	1.359(3)	1.290(3)	1.451(4)	1.350(2)	1.399(4)	13, 14
$[CuL(bipy)]ClO_4$	1.739(5)	1.337(6)	1.328(6)	1.374(5)	1.281(6)	1.460(7)	1.354(6)	1.335(6)	15
$[CuL(sacc)(H_2O)]\cdot 0.5H_2O$	1.721(10)	1.327(12)	1.340(13)	1.358(10)	1.285(13)	1.451(14)	1.362(12)	1.314(13)	16
$[CuL(bipy)][sacc]\cdot 2H_2O$	1.736(3)	1.338(4)	1.329(4)	1.358(4)	1.292(4)	1.459(4)	1.344(4)	1.335(4)	16
$[NiL_2]$ (1)	1.724(1)	1.352(9)	1.308(10)	1.370(8)	1.260(10)	1.458(10)	1.362(10)	1.356(9)	17
(2)	1.739(8)	1.335(10)	1.326(11)	1.342(8)	1.285(11)	1.445(11)	1.361(11)	1.339(9)	17
$[CoL_2]NO_3$	1.78(3)	1.40[b]	1.39[b]	1.36[b]	1.28[b]	1.53[b]	1.40[b]	1.43[b]	18
	1.77(3)	1.40[b]	1.37[b]	1.34[b]	1.29[b]	1.42[b]	1.48[b]	1.45[b]	
$[CdL_2]$	1.74(1)	1.36(1)	1.33(1)	1.36(1)	1.28(1)	1.46(2)	1.36(1)	1.35(2)	6
$[TlMe_2(L)]$ (molecule 1)	1.733(8)	1.38(1)	1.32(1)	1.370(8)	1.271(8)	1.48(2)	1.35(1)	1.34(1)	*c*
(molecule 2)	1.726(7)	1.364(9)	1.328(9)	1.362(8)	1.276(8)	1.46(1)	1.339(9)	1.34(2)	*c*

	S(1)–C(1)–N(1)	N(1)–C(1)–N(2)	S(1)–C(1)–N(2)	C(1)–N(2)–N(3)	N(2)–N(3)–C(2)	N(3)–C(2)–C(3)	C(2)–C(3)–N(4)	Ref.
HL·H_2O	124.1(2)	117.8(3)	118.1(2)	119.3(3)	114.7(3)	121.2(3)	114.6(3)	12
$[\{Cu(HL)(SO_4)_2\}_2]$	122.7(2)	115.8(2)	121.5(2)	116.1(2)	122.3(2)	115.1(2)	114.4(2)	13
$[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$	121.4(3)	116.9(3)	121.6(2)	116.1(3)	120.8(3)	114.9(3)	114.6(3)	11
$[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$	121.3(3)	117.1(3)	121.6(2)	116.6(2)	126.8(3)	114.2(3)	114.4(3)	11
$[CdCl_2(HL)]\cdot H_2O$	120.9(3)	114.8(3)	124.2(3)	119.3(3)	119.1(3)	117.2(3)	117.5(3)	6
$[\{CuL(MeCO_2)\}_2]$	118.7(2)	116.5(2)	124.8(2)	111.7(2)	119.3(2)	116.3(2)	115.6(2)	13, 14
$[CuL(bipy)]ClO_4$	117.7(4)	117.0(4)	125.2(4)	111.6(4)	119.7(4)	115.9(4)	114.4(4)	15
$[CuL(sacc)(H_2O)]\cdot 0.5H_2O$	118.2(8)	117.2(9)	124.6(8)	110.4(8)	118.8(9)	117.5(10)	113.4(10)	16
$[CuL(bipy)][sacc]\cdot 2H_2O$	118.6(2)	116.5(3)	124.9(2)	111.4(2)	119.4(3)	115.9(3)	115.3(3)	16
$[NiL_2]$ (1)	117.2(0.6)	116.3(0.7)	126.5(0.6)	112.8(0.6)	118.2(0.6)	119.8(0.7)	113.7(0.7)	17
(2)	117.2(0.6)	116.3(0.7)	126.5(0.6)	112.8(0.6)	118.2(0.6)	119.8(0.7)	113.7(0.7)	18
$[CoL_2]NO_3$	118[b]	119[b]	122[b]	111[b]	116[b]	114[b]	110[b]	18
	114[b]	122[b]	123[b]	111[b]	115[b]	110[b]	113[b]	
$[CdL_2]$	116.7(8)	115.5(9)	127.7(8)	115.3(8)	116.1(8)	118.0(9)	118.2(9)	6
$[TlMe_2(L)]$ (molecule 1)	116.1(6)	114.4(7)	129.5(6)	114.5(6)	115.1(6)	121.1(7)	117.0(8)	*c*
(molecule 2)	116.4(5)	116.7(6)	127.0(6)	114.1(6)	114.7(6)	120.1(6)	118.6(6)	*c*

[a] bipy = 2,2′-Bipyridine; Hsacc = saccharin. [b] Calculated from atomic fractional coordinates given in ref. 18. [c] This work.

Table 5 Proton NMR spectral data of the ligand and complexes at room temperature[a]

	δ[b]		
Compound	HL[c]	[HgMe(L)][d]	[TlMe$_2$(L)][d]
N(1)H$_2$	8.37 (br s, 1 H) 8.10 (br s, 1 H)	5.97 (vbr s) 5.24 (br s) } (2 H)	5.52 (br s, 2 H)
N(2)H	11.65 (s, 1 H)	—	—
C(2)H	8.07 (s, 1 H)	8.25 (s) 8.54 (s) } (1 H)	8.41 (br s)[e]
C(4)H	8.26 (d, 1 H)	7.93 (dt) 7.73 (m) } (1 H)	7.38 (d, 1 H)
C(5)H	7.79 (t, 1 H)	7.71 (m) 7.67 (m) } (1 H)	7.81 (td, 1 H)
C(6)H	7.34 (t, 1 H)	7.23 (m) 7.31 (m) } (1 H)	7.30 (t, 1 H)
C(7)H	8.53 (d, 1 H)	8.68 (m) 8.61 (m) } (1 H)	8.41 (br s)[e]
Me	—	0.83 (s)	0.77 (d)
J(^{1}H–M)[a]	—	182.7	386.2

[a] Numbering scheme in Fig. 1. Chemical shifts in ppm, coupling constants in Hz. [b] Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad, v = very. Number of protons calculated by integration. [c] In $(CD_3)_2SO$. [d] In $CDCl_3$ [e] The signals of these protons merge in one broad signal integrating for two protons.

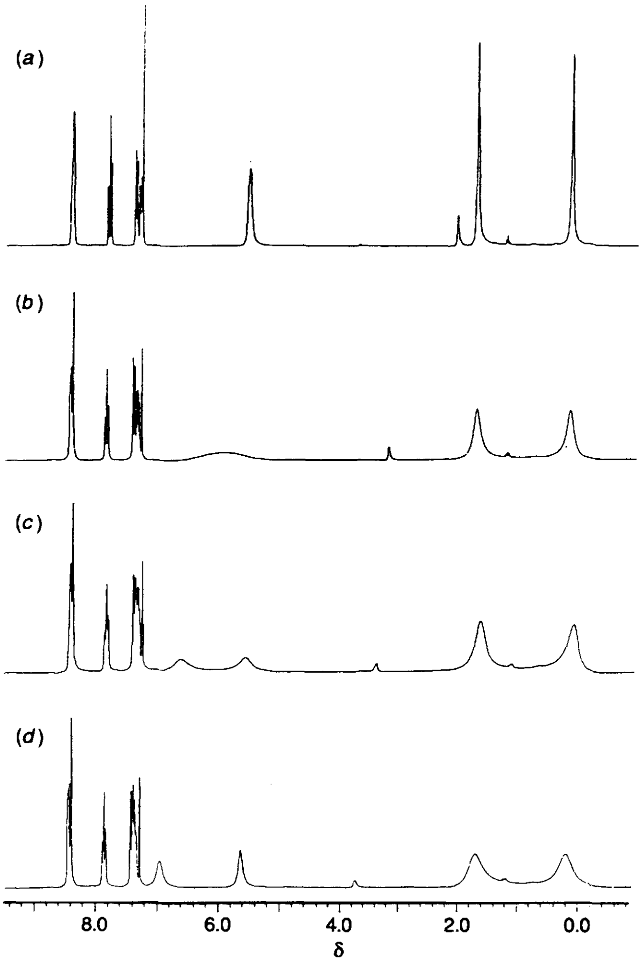
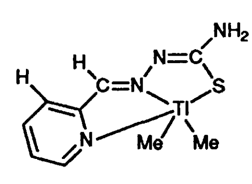


Fig. 3 Proton NMR spectra of [TlMe$_2$(L)] at (*a*) 293, (*b*) 243, (*c*) 233 and (*d*) 223 K



bond distances for the thiocarbamide group [SC(1)N(1)N(2)] indicate that metallation shifts the C(1)–S toward its thiol form and bond multiplicity from C(1)–N(1) towards C(1)–N(2); simultaneously, the angle S(1)–C(1)–N(2) widens while S(1)–C(1)–N(1) narrows, probably due, at least in part, to the displacement of the π charge. The angle C(1)–N(2)–N(3) narrows due to the bonding electrons of the N(2)–H bond becoming a lone pair on N(2). Finally, the angles N(2)–N(3)–C(2) and N(3)–C(2)–C(3) seem able to widen and narrow respectively in order to facilitate the proximity of N(4) to the metal, the extent of the change possibly being dependent on the size of the metal atom. In the dimethylthallium complex the radius of thallium seems to fit well with the values of these angles in HL·H$_2$O, almost no change being observed when thallation occurs.

IR Spectroscopy.—The changes in the thiosemicarbazone bands of the HL spectrum[19] suggest S,N co-ordination in both complexes.[7b] Of the pyridine bands that are useful for diagnosis of co-ordination (those located at 1585, **1035**, **995**, 745, **720** and **615** cm^{-1} for HL[20]), some are masked by the thiosemicarbazone vibrations in [TlMe$_2$(L)], but those listed in bold shift to higher wavenumbers (1050, 730 and 640 cm^{-1}) in keeping with the N(4), or N(14), co-ordination observed in the X-ray study. For [HgMe(L)], on the other hand, these bands remain at the same positions as in HL, ruling out co-ordination of the pyridine ring to the mercury atom.

^{1}H *NMR Spectroscopy.*—Although HL is not soluble in $CDCl_3$ its complexes are. The chief spectral data for [TlMe$_2$(L)] and [HgMe(L)] in this solvent are listed in Table 5, which for comparison also includes data for HL in $(CD_3)_2SO$. The spectrum of the thallium complex at various temperatures (Fig. 3) exhibits differences from the ligand spectrum that cannot be due to the change in solvent. Deprotonation and metallation of HL suppress the highest-frequency signal from its

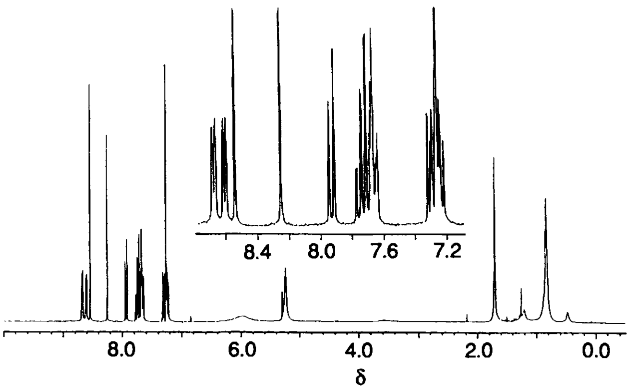
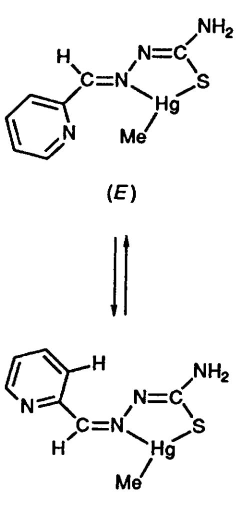


Fig. 4 Proton NMR spectrum of [HgMe(L)] at room temperature



(*E*)

(*Z*)

spectrum (Table 5), while the signals for C(2)–H and C(7)–H merge in a broad band at δ 8.41. Even more revealingly, the C(4)–H proton is strongly shielded, its signal in the complex being located at a lower frequency than that of the C(5)–H proton instead of at a higher frequency as for the ligand. This transposition can be related to the structural arrangement of the ligand in the thallium complex. In the (*E*) isomer of HL the C(4) proton is deshielded because a certain rotational conformation places it under the deshielding influence of the magnetic anisotropy of N(3) and the C(2)=N bond.[21] No such deshielding is possible in the thallium complex if N(4) is bound to the metal. Hence the observed displacement of the C(4)–H signal toward lower frequencies suggests that, in $CDCl_3$ solution as in the solid state, the thallium atom is co-ordinated to the pyridine N.

Fig. 3(*a*) also shows that, at room temperature, the protons of the NH_2 group become magnetically equivalent in $[TlMe_2(L)]$, possibly due to partial loss of C(1)–N(1) bond multiplicity suggested by the observed changes in bond distances (see above). The NH_2 signal broadens when the temperature is lowered [Fig. 3(*b*)], and finally splits into two broad bands [Fig. 3(*c*)] which become sharper and clearly separate as the temperature is further lowered until the complex eventually precipitates [Fig. 3(*d*)]. These results suggest that the C(1)–N(1) bond retains enough multiplicity to prevent free rotation about this bond at low temperature, thus placing one of the amino hydrogens under the deshielding influence of the C(1)–N(2) group. Other spectral changes observed on cooling include the expected[22] broadening of the signals of the organometallic methyl groups, slight alterations in the pattern of the pyridine ring protons, and the splitting of the broad signal of highest frequency [Fig. 3(*a*)–(*d*)].

The spectrum of [HgMe(L)] (Fig. 4) is more complex suggesting the presence of more than one isomer. If the arrangement observed in other thiosemicarbazonates holds in [HgMe(L)] [an assumption supported by the value of $^2J(^1H-^{199}Hg)$ (Table 5), which is very close to that observed for (cyclopentanone thiosemicarbazonato)methylmercury(II)[7a]], then co-ordination *via* N(4) is ruled out by the steric hindrance of the methyl group, and cannot favour the C(2)–N(3) (*E*) isomer as it does in $[TlMe_2(L)]$. The presence of both (*E*) and (*Z*) isomers explains the splitting observed in Fig. 4, where the clearly split signals have been attributed to the corresponding isomer on the basis of spectral data for the free ligand.[6] Special considerations must again be applied to C(4)–H: though in (*Z*)-HL this proton is more shielded than in (*E*)-HL,[21] it would appear to be only the (*Z*) isomer of the complex that places it under the deshielding influence of the magnetic anisotropy of C(2)=N(3) and N(3), and the signal located at higher frequency has therefore been attributed to the (*Z*) isomer. The methylmercury signal is broad but unique, suggesting a fast interchange of the organometallic cation between (*E*) and (*Z*) ligand molecules.

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