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Methyl- and Phenylmercury(II) Derivatives of 2-Mercaptobenzothiazole. Crystal Structure of (2-Mercaptobenzothiazolato)methylmercury(II)

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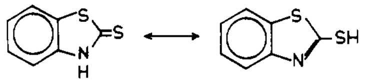
The complexes MeHgL and PhHgL (HL = 2-mercaptobenzothiazole) have been obtained from the reaction of the ligand with methylmercury hydroxide and phenylmercury acetate, respectively, in methanol. MeHgL, which has been characterized by single-crystal X-ray diffraction analysis (crystal data: triclinic, space group $P\bar{1}$, with $a = 8.009$ (4) Å, $b = 10.042$ (4) Å, $c = 13.074$ (3) Å, $\alpha = 101.25$ (2)°, $\beta = 102.61(3)$°, $\gamma = 101.42$ (3)°, $R = 0.067$), crystallizes with two independent molecules, I and I′, contained in each asymmetric unit with a coordination geometry based on the almost linear C–Hg–S group (Hg–S = 2.369 (6) Å, Hg–C = 2.06 (2) Å, and C–Hg–S = 177.7 (7)° for I; Hg–S = 2.375 (6) Å, Hg–C = 2.10 (3) Å, and C–Hg–S = 178.8 (6)° for I′). A secondary intramolecular interaction between the mercury atom and the C=N group of the ring and some weak intermolecular interactions between the metal and sulfur atoms were also found. The vibrational spectra of this compound and the phenylmercury(II) compound are discussed in light of the crystal structure. Diagnostic criteria of the bonding modes for the ligand are assessed.

Introduction

In structural studies there has been increasing interest in the analysis of "secondary bonds"[2] intermediate in strength between covalent and van der Waals bonds. Attention has been drawn to their possible relevance to the mobility of the methylmercury(II) ion in biological systems.[3] Although their origin is not fully understood at the orbital level,[4] they have been detected in methylmercury(II) compounds both in the solid state and in solution,[5] so that the coordination of the CH_3Hg^+ cation may be more complex than simple linear bicoordination. Less information is available concerning phenylmercury(II) compounds, but in these too, secondary bonds have been detected in the solid state.[2]

As a part of a program of research into these weak bonds in the complexes of organometallic cations, we have prepared the 2-mercaptobenzothiazole (HL) derivatives of methyl- and phenylmercury(II). This ligand (see eq 1), which adopts the thione



(1)

form in the solid state,[6] and possibly in solution also,[7] readily enters into complexes that can be cations $[M(HL)_n{}^{m+}]$, anions $(ML_n{}^{m-})$ or simple or mixed neutral adducts (ML_n or ML_nL_m').[8] Interest in this ligand derives from its biological activity and from its applications as an analytical reagent, a rubber accelerator, and an anticorrosion agent. Its use on silica gel for chromatographic concentration of mercury and organomercury(II) compounds in sea water has also been proposed.[9]

Most of the structural conclusions regarding mercaptobenzothiazole complexes have been based on the changes induced in the IR spectrum by complexation. Since the unreliability of this method has been pointed out,[10] X-ray determination of structures are highly desirable to confirm or deny reported structures. The present study describes the determination of the structure of CH_3HgL by X-ray diffraction and the presence of what seems to be a secondary interaction of methylmercury(II) with a C=N double bond. The vibrational evidence for the change in the tautomeric equilibrium (1) due to complexation is also presented, and the likelihood of the existence of the secondary bond in solution, in solvents that are poor donors, is discussed.

Experimental Section

Methylmercury(II) chloride (ROC/RIC), phenylmercury(II) acetate (Fluka, "purum") and 2-mercaptobenzothiazole (Aldrich) were used as received. Microanalysis for C and H on the complexes prepared were performed by Galbraith Laboratories, Inc., Knoxville, TN. Mercury was determined by using a Varian AA-6 atomic absorption spectrometer after digestion of compounds with a mixture of sulfuric and nitric acids. The molecular weights were measured in benzene with a Knauer vapor pressure osmometer, and the conductivity data (in acetonitrile) were obtained with a WTW conductivimeter. Dipole moments were determined in benzene at 25 °C as reported previously.[11] IR spectra were recorded in Nujol mulls or pressed KBr disks on a Perkin-Elmer 180 spectrometer, and Raman spectra were recorded on a Jarrell-Ash 500 spectrometer (Ar^+ laser, 5145 Å). ^{13}C NMR spectra in $CDCl_3$ or Me_2SO solutions were recorded on a Bruker WM 250 apparatus.

Preparation of Complexes. MeHgL. A solution of methylmercury hydroxide was obtained by stirring MeHgCl (1.303 g, 0.008 mmol) with an excess of freshly precipitated silver oxide for 48 h in deionized water. The resulting solution, once filtered, was mixed with 0.820 g (0.005 mmol) of 2-mercaptobenzothiazole in methanol. The yellow solid formed was removed by filtration, washed with water, and recrystallized from ethanol under slow evaporation until crystals suitable for crystallographic analysis were obtained. (Anal. Calcd for $C_8H_7HgNS_2$: C, 25.2; H, 1.8; Hg, 52.5. Found: C, 25.4; H, 2.0; Hg, 51.7.) Mp: 112–113 °C.

PhHgL. Solutions of phenylmercury(II) acetate (1.810 g, 0.005 mmol) in ethanol and 2-mercaptobenzothiazole (0.683 g, 0.005 mmol) in the same solvent were mixed, and a white precipitate formed. The solvent was removed by filtration, and the solid was redissolved in hot ethanol. Crystals were obtained by slow evaporation. (Anal. Calcd for $C_{13}H_9HgNS_2$: C, 35.2; H, 2.0; Hg, 45.2. Found: C, 35.2; H, 2.0; Hg, 44.8.) Mp: 151–152 °C.

X-ray Structure Analysis. Table I shows experimental data. A light yellow single crystal was selected by examination under polarized light and used on a Enraf-Nonius CAD-4 diffractometer for cell dimensions measurement and intensity data collection at room temperature. Possible space groups were $P1$ and $P\bar{1}$. The choice of $P\bar{1}$ was confirmed by

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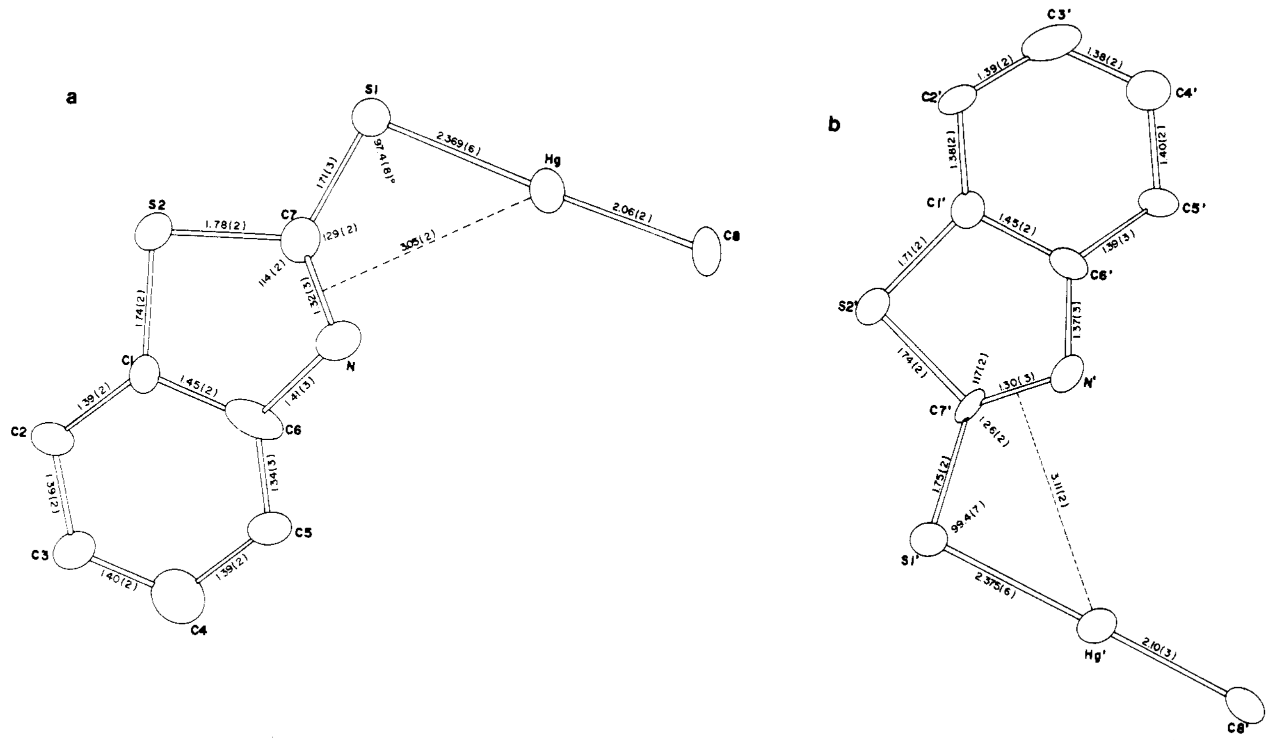

Figure 1. ORTEP drawing of MeHgL showing the molecular structure and labeling scheme: (a) molecule I; (b) molecule I′ (see text).

Table I. Experimental Data for X-ray Diffraction Study

	A. Crystal Parameters
formula	$C_8H_7HgNS_2$
cryst syst	triclinic
space group	$P\bar{1}$
cell params (at 290 K)	a = 8.009 (4) Å b = 10.042 (4) Å c = 13.074 (3) Å α = 101.25 (2)° β = 102.61 (3)° γ = 101.42 (3)° V = 974 (1) Å^3 Z = 4 molecules/cell (2 molecules/asym unit)
cryst shape	parallelepipedal
boundary faces	(100), (010), (001)
dist, mm	0.187, 0.175, 0.081
cryst vol	0.020 mm^3
d_{obsd}	2.65 g cm^{-3}
d_{calcd}	2.745 g cm^{-3}
μ	155 cm^{-1}
min, max transmission factors	0.0306, 0.1313
	B. Intensity Data
radiation	graphite-monochromated Mo Kα (λ = 0.709 Å)
takeoff angle	3°
data collcn proc	zigzag
θ_{limits}	1.0–24.0°
$\pm h,\pm k,\pm l$	h = −8, +8; k = −11, +11; l = −5, +14
scan mode	θ–2θ
scan range	0.80°
scan speed	4.023 to 6.705° min^{-1}
std reflcns	$(1\bar{1}\bar{4})$ $(20\bar{2})$ $(31\bar{2})$
no. of reflcns collcd	3662
no. of unique data used	2888, of which 1939 with $F_o > 3\sigma(F_o^2)$
final R values	R = 0.067, R_w = 0.069, R_{all} = 0.104

successful determination of the structure in this space group. The cell dimensions were obtained by least-squares minimization of the setting angles of 25 reflections. A total of 3662 reflections were measured and corrected for Lorentz, polarization, and absorption effects, reduced to observed structure factors, and merged. After processing, there were only 2888 unique reflections, of which 1939 with $F_o^2 > 3\sigma(F_o^2)$ were used in the structure analysis. The agreement factor between measured equivalent reflections R_i was 0.03.

Table II. Positional and Thermal Parameters

atom	x/a	y/b	z/c	B_{iso}, Å^2
CC8	0.140 (3)	0.362 (2)	0.031 (2)	4.3 (7)
Hg	0.0041 (1)	0.2163 (1)	0.0947 (1)	4.23 (3)
SS1	−0.1619 (9)	0.0523 (7)	0.1657 (5)	4.4 (2)
CC7	−0.010 (3)	−0.044 (2)	0.189 (2)	3.6 (6)
SS2	−0.0479 (8)	−0.1649 (6)	0.2702 (5)	3.8 (2)
NN1	0.137 (3)	−0.038 (2)	0.159 (2)	4.3 (6)
CC6	0.224 (3)	−0.139 (2)	0.190 (2)	5.0 (7)
CC1	0.143 (3)	−0.216 (2)	0.258 (2)	3.0 (5)
CC2	0.208 (3)	−0.322 (2)	0.293 (2)	4.0 (6)
CC3	0.366 (3)	−0.337 (3)	0.269 (2)	5.6 (9)
CC4	0.449 (3)	−0.259 (2)	0.209 (2)	5.4 (7)
CC5	0.377 (3)	−0.157 (2)	0.171 (2)	3.9 (6)
C8′	−0.296 (4)	0.019 (3)	0.457 (2)	5.7 (8)
Hg′	−0.0934 (1)	0.1701 (1)	0.4342 (1)	4.29 (3)
S1′	0.1354 (9)	0.3370 (7)	0.4053 (5)	4.6 (2)
C7′	0.217 (2)	0.447 (2)	0.536 (2)	3.0 (5)
S2′	0.3732 (8)	0.6030 (6)	0.5531 (5)	4.2 (2)
NN′	0.168 (2)	0.425 (2)	0.621 (2)	3.6 (5)
C6′	0.264 (3)	0.531 (2)	0.709 (2)	3.4 (6)
C1′	0.390 (3)	0.641 (2)	0.689 (2)	3.9 (6)
C2′	0.492 (3)	0.756 (2)	0.771 (2)	4.1 (6)
C3′	0.472 (4)	0.759 (3)	0.874 (2)	7 (1)
C4′	0.356 (3)	0.656 (2)	0.897 (2)	5.1 (8)
C5′	0.250 (3)	0.540 (2)	0.814 (2)	3.7 (6)

Solution and Refinement of the Structure. The Hg coordinates were determined by the Patterson method and those of the remaining nonhydrogen atoms by successive difference Fourier electron density calculations. Anisotropic full-matrix least-squares refinement was performed, taking in consideration only one of the independent molecules in each alternating cycle, until all parameter shifts were smaller than their standard deviations. At this point a final R = 0.067 and R_w = 0.069 were obtained. The minimization function used was $w(k|F_o| - |F_c|)^2$ where w is a weighting function given by $1/(\sigma^2(F_o) + 0.0045F^2)$ and $\sigma(F_o)$ is the standard deviation of F_o taking in account only the counting statistics. All calculations were done by using the SHELX-76[12] program package, except the refinement of cell dimensions and Lp correction, which were done with the Enraf-Nonius structure determination package.[13] Complex neutral atomic scattering factors were taken from ref 14.

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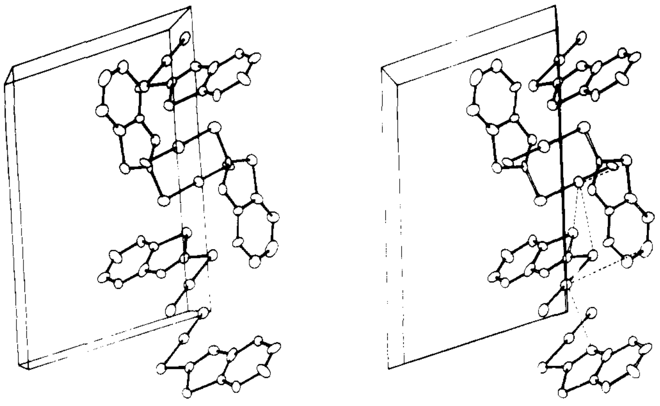

Figure 2. Stereoscopic view of the molecular packing for MeHgL. Broken lines show closest intermolecular distances for mercury atom.

Table IV. Important Intermolecular Distances (Å)

Hg-N[a]	3.28 (3)	Hg′-S1[b]	3.363 (7)
Hg-S1′[b]	3.844 (6)	Hg′-S2[b]	3.751 (6)
Hg-C4′[c]	3.39 (3)	Hg′-S2[d]	3.797 (7)
Hg-Hg[a]	4.764 (1)	Hg′-S2′[c]	3.504 (7)

[a] −x, −y, −z. [b] x, y, z. [c] −x, 1 − y, 1 − z. [d] −x, −y, 1 − z.

Final positional and equivalent isotopic thermal parameters of all non-hydrogen atoms are listed in Table II. The anisotropic thermal parameters are shown in Table III, which is available as supplementary material along with a table of the complete observed and calculated structure amplitudes.

Results and Discussion

Crystal and Molecular Structure of MeHgL. Figures 1 and 2 show the most important structural parameters of the two independent molecules, I and I′, contained in each asymmetric unit. I and I′ can be considered to be planar, their least-squares planes are given by $-0.1826x + 0.4180y + 0.8899z + 1.6484 = 0$ and $-0.7816x + 0.5983y - 0.1763z + 1.0303 = 0$, respectively. The dihedral angle between the molecular planes is 87.2°.

The ligand coordinates via the deprotonated thiol group. The C–S distances are rather shorter than the theoretical value for a single C–S bond (1.78 Å[2]), especially in I′, which may mean a degree of conjugation between this bond and the ring (see below). The S–Hg and C–Hg distances are quite normal. The mercury atom is almost equidistant from the doubly bonded carbon and nitrogen atoms. It is slightly over 3 Å from the midpoint of this bond, and its distance from the nitrogen atom, while less than the sum of the van der Waals radii (using Canty and Deacon's value for r_{vdW} of mercury[15]) is nevertheless greater than that found in similar compounds.[16-18] This suggests that there is a secondary interaction between the mercury atom and the π orbital of the C=N bond. Secondary bonding between the mercury and the carbon–carbon bond of the benzene ring has already been reported in methyl(L-tyrosinato)mercury(II),[19] and Bach et al.[20] have postulated reaction mechanisms involving interaction between the methylmercury(II) cation and the π orbital of alkenes.

Table IV shows some intermolecular distances involving the metallic atom of I and I′. The only sulfur atom that is close to the mercury of I and does not belong to I is S1′, the thiol sulfur of the other molecule of its own asymmetric unit, and since the sum of the van der Waals radii of Hg and S is 3.5 Å,[15,21] it lies too far away [3.844(6) Å] for coordination. The metallic atom of molecule I′, on the other hand, has two S2 (ring sulfurs of another symmetry-related molecule I) atoms at distances of 3.751 and 3.797 Å, one S1 (the thiol sulfur of I) atom at 3.363 Å, and one S2′ (the ring sulfur of molecule I′ of another asymmetric unit) atom at 3.504 Å. Note that although the S2′ distance is at the limit of the sum of the van der Waals radii, it is within the range considered close contact in $CH_3Hg(pen)H_2O$.[22] So, molecule I is practically an isolated unit within the lattice while molecule I′ presents some intermolecular interactions, as an ORTEP[23] stereoscopic view of the molecular crystal packing, given in Figure 2, shows.

Vibrational Spectra. Analysis of the changes brought about in the spectra of the ligand upon coordination is hindered by the simultaneous thione–thiol (eq 1) electronic ring reordering. Furthermore, the vibrations of interest for the analysis of the complexes, ν(C=N) and ν(C=S), are not pure but just two of the several contributions to the thioamide I, II, III, and IV bands associated with the HNCS group.[10] Therefore, the stretching C=C and C=N ring vibrations of the complexes are compared below both with those of the ligand and with those of bis(2-benzothiazolyl)disulfide (L-L). The changes in bands shown by "selenation" to contain ν(C=S) contirbutions[10] are also considered.

Table V lists the most significant bands in the range 1600–1400 cm^{-1} showing that the absorption patterns of the organomercury complexes resemble that of the L-L more than that of HL. The weak signal at 1560 cm^{-1}, which is also present in L-L and is stronger in the Raman spectrum, has been assigned[24] to ν(C=N) and is unaffected by changes in the metallic moiety, as is shown by its appearing in the same position in L-L, MeHgL, PhHgL, AgL_2,[24] and Me_2TlL.[25] In the mercury derivatives all the three bands in the region of 1500–1400 cm^{-1} are shifted to lower wavenumbers than in the disulfide, and the shifts are similar in both complexes, suggesting that these vibrations are to some extent diagnostic of coordination.[26] Of the bands with C=S contributions,[10] the one located at 300 cm^{-1} in the IR spectrum of HL vanishes totally in L-L, and in the complexes, those situated at 1030 (vs) and 605 (s) cm^{-1} undergo shifts to lower wavenumbers and the others [1010 (s), 525 (w), and 395 (m) cm^{-1}] show a negligible shift.

In MeHgL, $\delta_{sym}(CH_3)$ appears at 1190 (IR) and 1194 cm^{-1} (Raman) and ν(Hg–C) at 545 cm^{-1} in both the IR and Raman spectra. They lie within the regions typical of coordination via sulfur atoms.[27] The medium band at 330 cm^{-1} in the IR spectrum (330 (s) cm^{-1}; Raman) has been assigned to ν(Hg–S), though it may be not a pure band.[27]

In phenylmercury(II) complexes, the "X-sensitive" band most affected by the coordination of the mercury atom seems to be the t mode,[28] which generally appears between 225 and 220 cm^{-1} in the IR spectrum.[29] The weak band at 242 cm^{-1} in the IR spectrum of PhHgL (245 (s) cm^{-1}; Raman) has been assigned to this mode. The relationship between the IR and Raman intensities of this band suggest that the Hg–S stretching mode lies at a higher wavenumber.[30] Although on this basis the strong 328-cm^{-1} IR band (335 (m) cm^{-1}; Raman) can be assigned to

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Table V. Most Important IR and Raman Bands (1600–1400 cm^{-1})

L		L-L		MeHgL		PhHgL	
IR	R	IR	R	IR	R	IR	R
1595 (s)	1590 (s)		1600 (w)		1590 (w)		1595 (w)
		1560 (w)	1565 (m)	1560 (w)	1565 (w)	1595 (w)	1570 (w)
						1555 (w)	
1500 (vs)	1450 (w)	1470 (vs)	1470 (vs)	1455 (s, sh)	1455 (s)	1455 (vs)	1465 (s)
1460 (vs)	1460 (m)	1455 (s)		1450 (s)	1450 (s)	1450 (s)	1460 (s)
1430 (vs)	1430 (mw)	1430 (vs)	1440 (vs)	1420 (vs)	1420 (vs)	1410 (vs)	1425 (vs)
1405 (m, sh)							

Table VI. ^{13}C NMR Spectra[a]

	L[b]	L-SCH$_3$[b]	MeHgL	MeHgL[c]	PhHgL[c]
C1	129.9	134.7	137.2	137.5	137.6
C2	121.8	121.3[d]	120.6[d]	121.9[d]	122.1[d]
C3	124.6	123.9	123.7	124.6	124.8
C4	127.5	126.0	125.7	126.8	127.0
C5	112.9	120.9[d]	120.4[d]	120.9[d]	121.1[d]
C6	141.6	152.9	152.9	154.0	154.0
C7	190.4	167.6	169.2	170.8	170.7
others				11.4 (Me)	154.0 (C–Hg)[e] 137.9 (C_o Ph) 129.5 (C_m Ph) 129.0 (C_p Ph)

[a] In ppm from Me$_4$Si and with CDCl$_3$ as solvent unless otherwise stated. [b] Reference 34. [c] In Me$_2$SO. [d] Assignment can be reversed. [e] Phenyl assignment as given in ref 36.

ν(Hg–S), the assignment must be made with the same caution as in the case of MeHgL.

Characteristics in Solution. The compounds are monomers in solution in benzene, as is shown by determinations of their molecular weights (calcd for MeHgL, 382; found, 364; calcd for PhHgL, 444; found, 421). The dipole moments in this solvent (MeHgL, 1.96 D; PhHgL, 1.51 D) are not much different from that of benzothiazole (1.41 D[31]), so that the moment of the SHgR fragment must be oriented in such a way that its effect on the dipole moment of the ligand is small. No semiquantitative structural approximations may be made because of the asymmetry of the ring (Figure 1). The low dipole moments are in line with the tendency of MeHgL and PhHgL to dissolve in solvents with low dielectric constants. Even in ionogenic solvents with moderately high dielectric constants, such as acetonitrile, the compounds are still un-ionized since the molecular conductivity for solutions approximately 10^{-3} M are less than 1 Ω^{-1} cm^2 mol^{-1}.[32]

In order to ascertain if the secondary intramolecular interaction detected in solid persists in solution, ^{13}C NMR spectra were obtained in appropriate solvents, a technique used before for detecting weak bonds in similar systems.[33] Table VI lists the signals of the ligand, of its S-methylated derivative, and of the complexes, with assignments as given by Faure et al.[34] On passing from HL to the methylated derivative, C7 undergoes heavy shielding as the result of the thione to thiol transition (eq 1), C5, C6, and to a lesser extent C1 are deshielded, and the remaining carbons are only very slightly altered. When MeHgL is compared with L–SCH$_3$, one can expect deshielding in the carbon atoms of the thioazole ring as a result of the inductive effect upon coordination to the metal atom. This assumption was confirmed in the C1 and C7 cases but not in the C6 case. This fact may be due to the persistence of the secondary interaction in chloroform solution (note that the C2 carbon in the pyridine ligand shows an upfield shift when the nitrogen atom acts as a donor[35]) or to the presence of some amount of complex N-bonded in equilibrium with the S-bonded form. The effect is not apparent in Me$_2$SO-d_6 solution.

Registry No. MeHgL (HL = 2-mercaptobenzothiazole), 97571-17-0; PhHgL (HL = 2-mercaptobenzothiazole), 97571-18-1; MeHgOH, 1184-57-2; 2-mercaptobenzothiazole, 149-30-4; phenylmercury(II) acetate, 62-38-4.

Supplementary Material Available: Tables of complete anisotropic temperature factors (Table III) and observed and calculated structure factors for I and I′ (11 pages). Ordering information is given on any current masthead page.

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