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Synthesis and molecular structures of methyl and phenylmercury(II) complexes with benzaldehyde-4,4-dimethylthiosemicarbazone

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ABSTRACT

The reactions of benzaldehyde-4,4-dimethylthiosemicarbazone (**LH**) with methyl and phenylmercury (II) chlorides in different conditions were investigated. From the methyl derivative, two complexes [HgMeClLH] (**1**) and [HgMeL] (**2**), were obtained working in ethanol in the absence or the presence of basic medium respectively. However, in the same conditions only the complex [HgPhL] (**3**) was isolated. The corresponding complex containing the neutral ligand [HgPhClLH] (**4**) was prepared in refluxing dicloromethane. Furthermore, in the presence of hydrochloric acid, HgPhCl undergoes a symmetrization reaction to afford $HgPh_2$ and $[Hg(LH)_2(\mu\text{-}Cl)_2HgCl_2]$, reported previously from the reaction with $HgCl_2$. Spectroscopic studies and X-ray structural analysis showed that the thiosemicarbazone is always SN coordinated, giving a distorted tetrahedral arrangement in complexes **1** and **4** and a distorted T-shaped stereochemistry around the mercury centre in complexes **2** and **3**.

1. Introduction

Organomercury compounds of the type HgRX (R = alkyl or aryl; X = halide or acetate) have received considerable attention over the last three decades mainly related to the search for biologically active compounds and versatile reagents in controlled transmetallation reactions [1,2]. However, the high affinity of organomercurials for thiols and their lipophilic nature make them highly toxic to living organism, causing irreversible damage to the central nervous system [3,4]. The methylmercury ion, is probably the most ubiquitous compound and one of the most dangerous pollutant agents for animals and humans [5,6]. Recent studies have indicated that the coordination of organomercury(II) ions by the donors so as the increase of the metal coordination from the usual linear dicoordination to higher coordination numbers is quite important in the activation of the Hg–C bond, both in the enzymatic degradation processes and laboratory chemical reactions [7,8]. Symmetrization is a general reaction of the organomercurials which allows the simultaneous formation of symmetric diorganomercurials HgR_2 and Hg(II) complexes [9]. Such reactions, involving the cleavage of an Hg–C bond, are promoted by strong complexing agents such as sulphur donors.

Thiosemicarbazones have been extensively studied due to their pharmacological properties and their coordinative behaviour towards transition metal ions [10–12]. However, very few mercury and organomercury complexes with thiosemicarbazone are known [9,13,14]. Moreover, they are promising ligands to detoxify organomercury(II) by activation of Hg–C bond using coordination, followed by treatment with acid, to generate parent hydrocarbon (RH) and inorganic mercury(II) salts [9,14].

In our group we explored the coordination behaviour of several potentially tetradentate bis(thiosemicarbazones) with mercury(II) salts and methylmercury(II) chloride. In the mercury(II) complexes, the ligands behave as tetradentate chelate [15] even in the case of hybrid thiosemicarbazone-hydrazone molecules [16,17], but in the complexes obtained by the reaction of benzil bis(thiosemicarbazide) with methylmercury the ligand was only bonded through the sulphur atom acting as a bidentate bridged donor [18]. In the triazine 3-thione derivatives the cyclic molecules were bonded to the mercury(II) and methylmercury(II) only by the sulphur atom giving a linear coordination to the metal centre [19]. We also studied the reactivity of the title molecule with mercury(II) salts (bromide, chloride, iodide and nitrate) and the results showed that the structures of the complexes depend on the counterion used. The ligand was a NS quelate except in a dinuclear iodine derivative containing bridged iodide in which the ligand was monodentate through the sulphur atom [20].

In this paper we report new complexes of benzaldehyde-4,4-dimethylthiosemicarbazone, LH, formed by reaction with HgRCl

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(R = Me or Ph). We obtained complexes with 1:1 Hg:LH ratio and with the ligand being neutral or deprotonated. The complexes were characterized using multinuclear NMR, IR and mass spectrometry. Three of the complexes were also characterized by single crystal X-ray diffraction.

2. Results and discussion

2.1. Synthesis of the complexes

Reaction of the ligand LH with HgMeCl in ethanol led to the obtaining of two complexes, [HgMeCl(LH)] (**1**) in neutral medium and [HgMeL] (**2**) when lithium hydroxide was used. By contrast, reaction of HgPhCl in ethanol without base induced the spontaneous deprotonation of the ligand to yield complex [HgPhL] (**4**), which was also obtained in the presence of lithium hydroxide. If some drops of hydrochloric acid were added to the reaction mixture to prevent ligand deprotonation, a symmetrization reaction took place and the complex $[Hg(LH)_2(\mu\text{-}Cl)_2HgCl_2]$, which was previously synthesized by reaction of LH with $HgCl_2$ [20], was obtained. Nevertheless, ligand deprotonation could be avoided in refluxing dichloromethane in which complex [HgPh(LH)Cl] (**3**) could be synthesized.

Mass spectra of the complexes confirmed the 1:1 ligand to metal stoichiometry. In the spectra of complexes **1** and **3** there was a peak corresponding to the fragment $[M-Cl]^+$ while in complexes **2** and **4** it corresponded to $[M + H]^+$. The calculated and experimental isotopic splitting patterns are identical (Fig. 1). In addition, in the spectra of complexes **1** and **2** a peak corresponding to the ligand, due to demetallation, is observed.

2.2. X-ray structures

Crystallographic data of complexes **1**, **2** and **4** are summarized in Table 1.

The crystal structure of complex **1** is made up of [HgMeCl(LH)] units (Fig. 2). The ligand is neutral and coordinates in a bidentate mode through the imine nitrogen and the sulphur atom, leading to the formation of a five-member chelate ring. The mercury atom is in a tetra-coordinate environment provided by the ligand, the methyl group and the chloride. The τ_4 parameter is 0.54 and therefore the metal is in an environment intermediated between tetrahedral and square planar ($\tau_4 = 1$ for Td and $\tau_4 = 0$ for SP) [21]. In the complex the ligand is significantly more buckled and the electronic delocalization is smaller than in the free ligand. There are hydrogen bonds between the NH and the Cl leading to the formation of dimers that are held together by S···S interactions (3.349 Å, S–S Van der Waals radium 3.6 Å), giving rise to chains running along the *b* axis. This complex represents the first example of an organomercury(II) compound crystallographically characterized with a thiosemicarbazone ligand in which the chloride atom is retained.

The X-ray analysis of complex **2** reveals the presence of [HgMeL] units, in which the metal is surrounded by a deprotonated ligand acting as bidentate chelate and the methyl group in a distorted T-shape environment (Fig. 3). In this complex the ligand is more planar due to deprotonation, which induces a larger charge delocalization.

Complex **4** consists of [HgPhL] units (Fig. 4). The metal is in a coordination environment similar to those of complex **2** formed by a bidentate deprotonated ligand and the phenyl group. Due to deprotonation the ligand is much more planar than in complex **1** or when it is uncoordinated [20].

In all the complexes the C–S distance (Table 2) is much longer than in LH, due the strength of the Hg–S bond. The Hg–N distances (Table 3) are in the range found in other mercury complexes with thiosemicarbazones [20,22–24].

In complexes **1** and **2** the H bound to iminic carbon atom C1 is placed in *Z* configuration to the hydrazinic nitrogen N2, and hence the phenyl ring is directed to the mercury centre. By contrast, in complex **4** the disposition is *E*, causing the phenyl ring is pushed

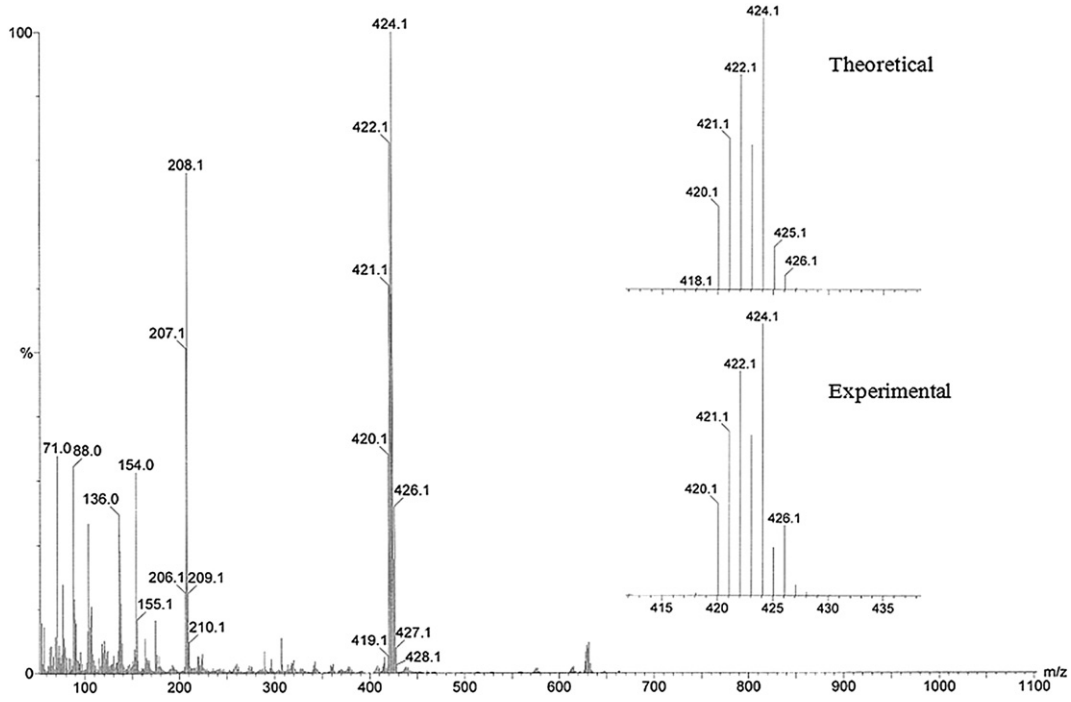

Fig. 1. FAB^+ mass spectrum of complex [HgMeCl(LH)] **1** including theoretical and experimental isotopic splitting pattern.

Table 1
Crystal data and structure refinement for **1**, **2** and **4**.

	1	**2**	**4**
Formula	$HgC_{11}H_{16}ClN_3S$	$HgC_{11}H_{15}N_3S$	$HgC_{16}H_{17}N_3S$
M	458.37	421.91	483.98
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	*P*-1	Pbca	P2(1)/*n*
a/Å	7.6427(7)	10.947(3)	16.961(4)
b/Å	9.3666(9)	7.2112(16)	5.4638(13)
c/Å	10.7236(9)	31.959(11)	17.498(4)
α/°	87.980(4)	90	90
β/°	70.785(4)	90	105.173(14)
γ/°	74.115(5)	90	90
U/Å^3	695.94(11)	1788.1(11)	4602.8(9)
Z	2	8	4
D_c/M g m^{-3}	2.187	2.222	2.054
Absorption coefficient mm^{-1}	11.382	12.344	9.964
F(000)	432	1584	920
Goodness of fit on F^2	1.127	1.372	1.098
Reflections collected	32,957	14,923	11,382
Independent reflections	3565 [*R*(int) = 0.0429]	2576 [*R*(int) = 0.0759]	2974 [*R*(int) = 0.0524]
Final *R*1and *wR*2 [$I > 2\sigma(I)$]	0.0192, 0.0507	0.0901, 0.2210	0.0311, 0.0730
Residual electron density (min, max) (e Å^{-3})	−0.895, 1.155	−7.249, 2.298	−1.197, 1.480

away from the phenyl ring bound to mercury, probably due to steric hindrance.

To date there were only eight three-coordinated phenylmercury complexes with a thiosemicarbazone ligand, and complex **2** is the first example of an analogous methylmercury derivative structurally characterized.

2.3. Infrared spectra

The band corresponding to ν(N–H) is observed in complexes **1** and **3** indicating that the ligand behaves as a neutral molecule, but it is absent in complexes **2** and **4**, confirming the ligand deprotonation. The coordination by sulphur induces a strong decrease in the ν(CS), as could be expected from the X-ray data. All the spectra show a band assigned to the ν(C–H), which is clearly shifted two lower wavenumbers than in LH, although the shift is much larger in complexes **2** and **4** in which the ligand has lost the acidic hydrogen atom.

2.4. NMR spectra

The new compounds were also characterized by NMR spectroscopy. In the ^{1}H NMR spectrum of complexes **1** and **3** the signal corresponding to the N–H group is clearly observed and therefore the ligand is neutral. By contrast, in the spectra of complexes **2** and **4** the signal has disappeared, confirming the ligand deprotonation. In complexes **1** and **2** can be observed a singlet at high field corresponding to the methyl group bound to mercury, while in complexes **3** and **4** a multiplet in the aromatic region due to the phenylmercury moiety can be observed.

All the ^{13}C NMR spectra were run in $CDCl_3$ solution except the one of complex **1**, which is not soluble enough, so ^{13}C CP/MAS NMR spectrum was recorded. In the spectra, the signals corresponding to the imine carbons and the thiocarbonyl groups are clearly shifted on complexation. The methyl groups bound to mercury in complexes **1** and **2** appear at 6.0 and 8.0 ppm respectively and the phenyl groups bound to mercury in compounds **3** and **4** are observed in the aromatic region.

The ^{199}Hg NMR is a useful tool to determine the metal environment, since the chemical shift is very sensitive to its coordination sphere. According to the literature, a decrease in the coordination number tends to give greater deshielding [14,25–28]. Electronegative substituents linked to mercury or to the atom next to mercury tend to increase ^{199}Hg nuclear shielding, whereas electropositive substituents cause deshielding [29]. Tetracoordinated complexes **1** and **3** exhibit resonances at −830.5 and −640.8 ppm respectively, while in three-coordinated complex **2** appears at −443.2 ppm. In the spectrum of complex **4**, also with coordination number of three, three signals can be observed, one at −317.3 ppm corresponding to the complex, one at −748.1 ppm corresponding to $HgPh_2$ [29] and the last one at −1403.0 ppm corresponding to $HgCl_2$ [28], indicating the partial symmetrization of the complex.

3. Experimental

IR spectra in the 4000–400 cm^{-1} range were recorded as KBr pellets on a Jasco FT/IR-410 spectrophotometer. Fast atom

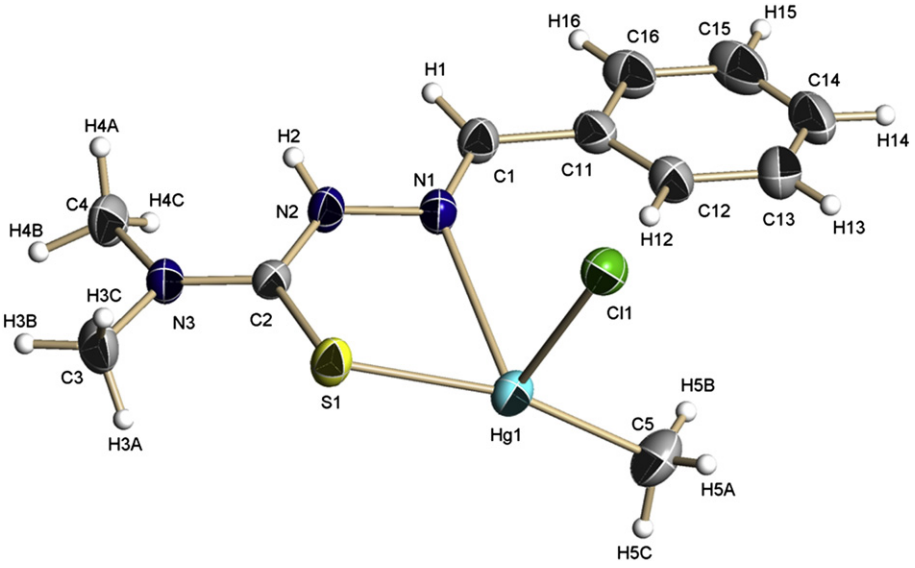

Fig. 2. Molecular structure of complex [HgMeCl(LH)] **1**. Thermal ellipsoids at 50% probability.

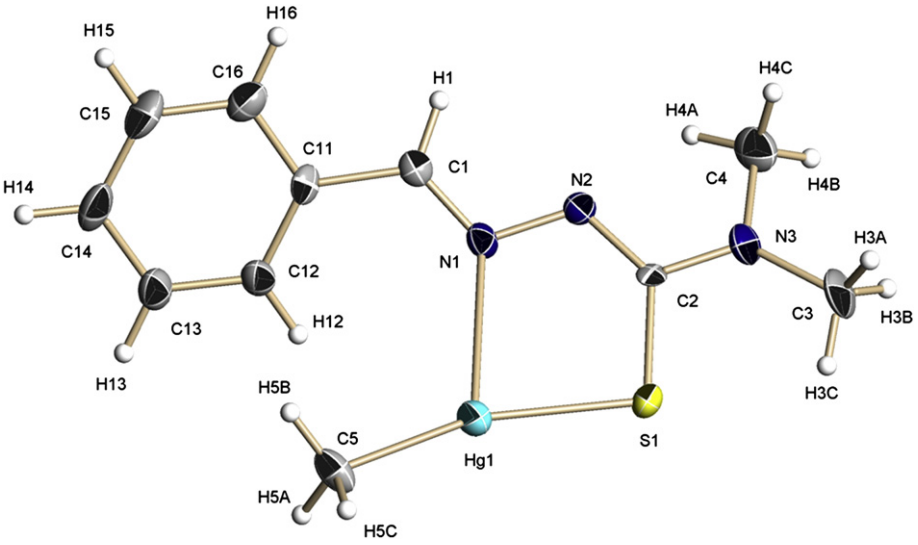

Fig. 3. Molecular structure of complex [HgMeL] **2**. Thermal ellipsoids at 50% probability.

bombardment (FAB) mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzylalcohol (*m*NBA) as the matrix. ^{1}H, ^{13}C and ^{199}Hg NMR spectra were recorded on a spectrometer Bruker AMX-300 using $CDCl_3$ or DMSO-d_6 as solvents and TMS (^{1}H and ^{13}C) or $HgMe_2$ (^{199}Hg) as internal reference. ^{13}C CP/MAS NMR spectra were recorded at 298 K in a Bruker AV400WB spectrometer equipped with a 4 mm MAS NMR probe (magic-angle spinning) and obtained using cross-polarization pulse sequence. The external magnetic field was 9.4 T, the sample was spun at 10–14 kHz and the spectrometer frequency was 100.61 MHz. For the recorded spectra a contact time of 4 ms and recycle delays of 4 s were used. Chemical shifts are reported relative to TMS, using the CH group of adamantane as a secondary reference (29.5 ppm).

3.1. Synthesis of the ligands and the complexes

All the reagents and solvents were commercially obtained and used without further purifications.

3.1.1. Benzaldehyde-4,4-dimethylthiosemicarbazone (*LH*)

The ligand LH was prepared by condensation of benzaldehyde and 4,4-dimethylthiosemicarbazide, following the procedure previously reported [20]. Anal. Calcd. for $C_{10}H_{13}N_3S$: C, 57.97; H, 6.28; N, 20.28; S, 15.46. Found: C, 57.94; H, 6.21; N, 20.25; S, 15.44. MS (FAB$^+$): *m*/*z* (%): 208.1 (100) $[M+H]^+$. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 9.00$ (s, 1H, NH), 7.71 (s, 1H, CH), 7.59 (m, 2H, Ph), 7.37 (m, 3H, Ph), 3.44 (s, 6H, CH_3) ppm. ^{1}H NMR (300 MHz, [D_6]DMSO, 25 °C): $\delta = 10.89$ (s, 1H, NH), 8.17 (s, 1H, CH), 7.62 (m, 2H, Ph), 7.41

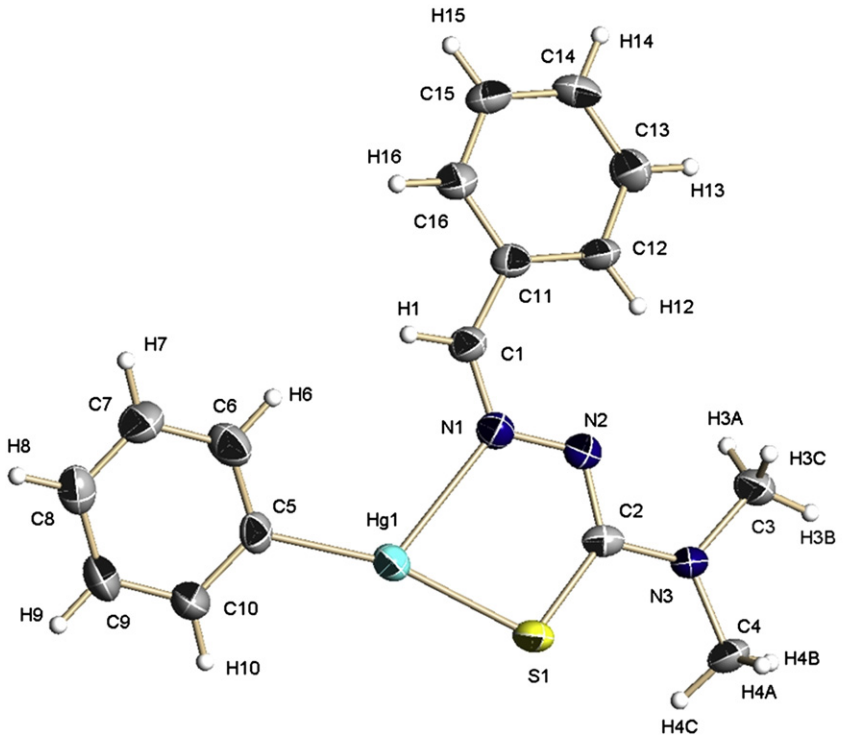

Fig. 4. Molecular structure of complex [HgPhL] **4**. Thermal ellipsoids at 50% probability.

Table 2
Selected bond distances (Å) of the ligand backbone in **LH** [20] and complexes **1**, **2** and **4**.

	LH	1	2	4
C(1)–N(1)	1.276(3)	1.272(4)	1.28(3)	1.310(7)
N(1)–N(2)	1.371(3)	1.388(3)	1.37(2)	1.364(7)
N(2)–C(2)	1.356(3)	1.342(4)	1.29(2)	1.328(8)
C(2)–N(3)	1.341(3)	1.326(4)	1.36(3)	1.352(8)
C(2)–S(1)	1.678(3)	1.724(3)	1.74(2)	1.757(6)

(m, 3H, Ph), 3.27 (s, 6H, CH_3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 181.8 (CS), 142.9 (CN), 134.1, 130.5, 129.2, 127.5 (Ph), 44.5 (CH_3) ppm. IR (KBr, cm^{-1}): ν(NH) 3229, ν(CH) 3165, $\nu(CH)_{Ph}$ 3009, $\nu(CH)_{Me}$ 2925, 2894, ν(CN) 1600, δ(HNCS) 1551, ν(CS) 1020.

3.1.2. [HgMeCl(LH)] (**1**)

To a solution of LH (0.100 g, 0.48 mmol) in ethanol (10 mL) solid HgMeCl (0.120 g, 0.48 mmol) was added and stirred at room temperature. Immediately a colourless solution was formed and after 2 h a white solid was obtained which was filtered off and dried *in vacuo*. (0.19 g, 86%). MS (FAB$^+$): *m*/*z* (%): 424.1 (100) [M–Cl]$^+$ 208.1 (80) [LH + H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 10.62 (br s, 1H, NH), 8.33 (s, 1H, CH), 7.63 (m, 2H, Ph), 7.40 (m, 3H, Ph), 3.47 (s, 6H, CH_3), 0.98 (s, J_{Hg-H} = 198 Hz, 3H, $HgCH_3$) ppm. ^{13}C CP/MAS NMR: 170.2 (CS), 152.6 (CN), 132.5, 131.7129.1, 125.8 (Ph), 45.4, 43.2 (CH_3), 9.6 (CH_3Hg). ^{199}Hg NMR (300 MHz, $CDCl_3$ + DMF, 25 °C): δ = −830.5 ppm. IR (KBr, cm^{-1}): ν(NH) 3157, ν(CH) 3099, $\nu(CH)_{Ph}$ 3018, $\nu(CH)_{Me}$ 2996, 2916, ν(CN) 1601, δ(HNCS) 1577, ν(CS) 881. Single crystals suitable for X-ray diffraction analysis were obtained from the mother liquor.

3.1.3. [HgMeL](**2**)

A solution of LH (0.100 g, 0.48 mmol) and $LiOH\cdot H_2O$ (0.02 g, 0.48 mmol) in ethanol (10 mL) was mixed with solid HgMeCl (0.120 g, 0.48 mmol) at room temperature to yield a yellow solution. After stirring for 2 h a yellow solid was obtained which was filtered off and dried *in vacuo*. (0.14 g, 68%). MS (FAB$^+$): *m*/*z* (%): 422.9 (60) [M + H]$^+$ 208.0 (30) [LH + H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.60 (s, 1H, CH), 7.60 (m, 2H, Ph), 7.41 (m, 3H, Ph), 3.29 (s, 6H, CH_3), 0.56 (s, J_{Hg-H} = 177 Hz, 3H, CH_3Hg) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 169.8 (CS), 152.7 (CN), 134.7, 129.4, 128.4, 128.1 (Ph), 40.2 (CH_3), 8.0 ($HgCH_3$) ppm. ^{199}Hg NMR (300 MHz, $CDCl_3$, 25 °C): δ = −443.2 ppm. IR (KBr, cm^{-1}): ν(CH) 3029, $\nu(CH)_{Ph}$ 3018, $\nu(CH)_{Me}$ 2915, 2886, ν(CN) 1586, ν(CS) 877. Single crystals suitable for X-ray diffraction analysis were obtained from the mother liquor.

3.1.4. [HgPhCl(LH)] (**3**)

LH (0.100 g, 0.48 mmol) dissolved in dichloromethane (10 mL) was mixed with solid HgPhCl (0.152 g, 0.48 mmol). The yellow solution was refluxed for 6 h. The scarce amount of solid was filtered off and discarded. The yellow solution was evaporated to afford a yellow solid. (0.22 g, 88%). MS (FAB$^+$): *m*/*z* (%): 485.0 (100) [M–Cl]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 12.03 (br s, 1H, NH), 8.8 (s, 1H, CH), 8.2 (d, 2H, Ph), 7.6 (d, 3H, Ph), 7.5–7.1 (m, 5H, Ph), 3.4 (s, 6H, CH_3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 150.4 (CS), 137.6 (CN), 136.5, 132.8, 130.9, 130.3, 129.0, 128.9, 128.7, 128.3 (Ph), 42.9 (CH_3). ^{199}Hg NMR (300 MHz, $CDCl_3$ 25 °C): δ = −640.8 ppm. IR (KBr, cm^{-1}): ν(NH) 3163, $\nu(CH)_{Ph}$ 3091, 3033, $\nu(CH)_{Me}$ 2977, 2930, ν(CN) 1599, ν(CS) 923.

3.1.5. [HgPhL] (**4**)

Solid HgPhCl (0.152 g, 0.48 mmol) was added to a solution of LH (0.100 g, 0.48 mmol) in ethanol (10 mL). The mixture was stirred for 2 h at room temperature. The solid formed was filtered off, washed with Et_2O and dried *in vacuo*. (0.17 g, 73%). MS (FAB$^+$): *m*/*z* (%): 485.0 (50) [M + H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.6 (s, 1H, CH), 8.3 (d, 1H, Ph), 7.47 (M, 3H, Ph), 7.42–7.21 (m, 6H, Ph), 3.3 (s, 3H, CH_3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 153.5 (CS), 147.2 (CN), 137.6, 136.9, 131.5, 129.9, 129.6, 128.7, 128.2. 128.0 (Ph), 40.2 (CH_3) ppm. ^{199}Hg NMR (300 MHz, $CDCl_3$, 25 °C): δ = −317.3, −748.1, −1403.0 ppm. IR (KBr, cm^{-1}): ν(CH) 3048, $\nu(CH)_{Ph}$ 3018, $\nu(CH)_{Me}$ 2926, ν(CN) 1593, ν(CS) 930. Single crystals suitable for X-ray diffraction analysis were obtained from the mother liquor.

This complex was also obtained when the reaction was carried out in the presence of $LiOH\cdot H_2O$. When the reaction was carried out in the presence of 5 drops of HCl, the complex $[Hg(LH)_2(\mu\text{-}Cl)_2HgCl_2]$, which was previously synthesized from $HgCl_2$ [20], was obtained.

3.2. X-ray crystallography

Data for complexes **1**, **2** and **4** were acquired using a Bruker AXS Kappa Apex-II diffractometer equipped with an Apex-II CCD area detector using a graphite monochromator (Mo K_α radiation, λ = 0.71073 Å). The substantial redundancy in data allows empirical absorption corrections (SADABS) [30] to be applied using multiple measurements of symmetry-equivalent reflections. The raw intensity data frames were integrated with the SAINT program, which also applied corrections for Lorentz and polarization effects [31]. The software package SHELXTL version 6.10 was used for space group determination, structure solution and refinement. The structures were solved by direct methods (SHELXS-97) [32], completed with difference Fourier syntheses, and refined with full-matrix least squares using SHELXL-97 minimizing $\omega(F_0^2 - F_c^2)$. Weighted *R* factors (R_w) and all goodness of fit *S* are based on F^2; conventional *R* factors (*R*) are based on *F* [33]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The NH hydrogen atom in complex **2** was located in a difference Fourier map and its coordinate and isotropic thermal parameters subsequently refined. CH hydrogen atoms were positioned geometrically after each cycle of refinement. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library.

Table 3
Selected bond distances (Å) and angles (°) in complexes **1**, **2** and **4**.

	1	2	4
Hg(1)–N(1)	2.742(3)	2.603(17)	2.481(5)
Hg(1)–S(1)	2.3985(8)	2.380(5)	2.3749(17)
Hg(1)–C(5)	2.078(5)	2.09(2)	2.084(6)
Hg(1)–Cl(1)	2.9152(9)	–	–
C(5)–Hg(1)–N(1)	117.00(14)	119.4(8)	117.6(2)
C(5)–Hg(1)–S(1)	166.26(13)	165.3(7)	165.31(18)
S(1)–Hg(1)–N(1)	72.42(6)	75.3(4)	77.04(12)
C(5)–Hg(1)–Cl(1)	96.80(13)	–	–
S(1)–Hg(1)–Cl(1)	92.49(3)	–	–
N(1)–Hg(1)–Cl(1)	92.89(6)	–	–

4. Conclusions

Four new organomercury(II) complexes with a thiosemicarbazone ligand were synthesized. When the reaction of HgMeCl is carried out without the presence of a base in the reaction medium the ligand coordinates as a neutral molecule, while if lithium hydroxide is added the ligand deprotonates. The reaction of HgPhCl in ethanol and without a base induces spontaneous ligand deprotonation. If hydrochloric acid is added to avoid ligand deprotonation a symmetrization reaction takes place to yield

$[Hg(LH)_2(\mu\text{-}Cl)_2HgCl_2]$. Nevertheless, ligand deprotonation with HgPhCl can be prevented in dichloromethane.

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Appendix A. Supplementary material

CCDC 903843–903845 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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