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Mercury complexes with the ligand benzaldehyde-N(4),N(4)-dimethylthiosemicarbazone

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ABSTRACT

The Schiff base benzaldehyde-N(4),N(4)-dimethylthiosemicarbazone (**LH**) and its complexes $[Hg(NO_3)(LH)_2]NO_3$ (**1**), $[Hg(L)_2]$ (**2**), $[Hg(LH)_2(\mu\text{-}X)_2HgX_2]$ [X = Cl (**3**), Br (**4**)], $[HgI(LH)(\mu\text{-}I)_2HgI(LH)]$ (**5**) and $[HgI_2(LH)]$ (**6**) have been synthesized and characterized by IR, mass spectrometry, ^1H and ^{13}C NMR and by single crystal X-ray diffraction. All the complexes were obtained in ethanol and complex **2**, in which the ligand is deprotonated, in addition needs the presence of basic medium. From mercury(II) iodide two complexes with the same molar ratio but with different structures were isolated. In all the complexes the ligand acts as a NS chelate, except in complex **5** in which is only S-donor. The coordination number of the mercury ion and the structures of the complexes depend on the counterion. Complexes **1, 2** and **6** are monomeric species but with different coordination spheres: $N_2S_2O_2$ with a distorted octahedral arrangement in complex **1**, and N_2S_2 or NSI_2 in a pseudo-tetrahedral geometry in complexes **2** and **6**, respectively. However, **3**, **4** and **5** are binuclear complexes with two halido bridges, but they show two different structures. In **3** and **4**, each mercury ion has a different environment giving an asymmetric structure, one is bonded to two NS-ligands and two halido bridges in a distorted octahedral geometry, and the other one has a tetrahedral environment formed by four halido ligands. In complex **5** both mercury ions are equivalent with a SI_3 distorted tetrahedral coordination sphere, formed by one S-bonded ligand, one terminal iodido and two iodido bridges.

1. Introduction

Industrial and also dental use of mercury has led to significant environmental pollutions. In addition, atmospheric oxidation and also methylation to methylmercury in natural waters caused severe contamination *via* the food chain. Despite far-reaching efforts to reduce the pollution, even currently, metallic mercury used for small scale gold mining or gold ore processing is causing both acute and chronic poisoning [1–3].

Mercury(II) is known to affect the central nervous system and also has renal, gastrointestinal and hematologic toxicity [2]. The high affinity of Hg(II) for sulfur-containing biomolecules, in particular, proteins with cysteine residues, has been proposed to inhibit or deactivate the biological function of several enzymes [3,4]. Chelating agents such as D-penicillamine ($H_2Pen{=}HSC(CH_3)_2{-}CH(NH_3)^+COO^-$) and BAL (2,3-dimercaptopropanol) have been clinically used for detoxification and efficiently reduce plasma levels of mercury(II) [2–4]. Often, very stable forms include linear complexes with two sulfur ligands; nevertheless, the Hg–S bonds are labile and for higher coordination numbers the structures are flexible, often with distorted trigonal or tetrahedral coordination geometries [5–7].

Thiosemicarbazones have been extensively studied due to their pharmacological properties and their coordinative behavior towards transition metal ions [8–10]. However, very few mercury(II) complexes with thiosemicarbazones are known, although they are good candidates as chelating agents for this metal ion. Some of them are based on potentially tridentate ligands, such as 2-acetylpyridine thiosemicarbazone, 2-pyridineformamide thiosemicarbazone, benzaldehyde thiosemicarbazone or their N(4) substituted thiosemicarbazones [11–13]. Reaction of these thiosemicarbazones with Hg(II) halides give rise to five-coordinate compounds with formula $[Hg(LH)X_2]$ (X = Cl, Br or I) in which the coordination occurs through the pyridine and the azomethine nitrogen atoms and the thiocarbonyl group [14,15]. Although they are less known these thiosemicarbazones can also form binuclear or polynuclear complexes in which the sulfur or the halogen atom acts as a bridge between metal centers [11,12] and, in some cases, they also behave as S-monodentate ligands to form complexes with formula $[Hg(LH)_2X_2]$, where the mercury atom is in a tetrahedral arrangement [16,17]. Polymerization is rare and only one coordination polymer with a thiosemicarbazone ligand is reported [16]. In our group, we have explored the reactivity of a N_2S_2 bis(thiosemicarbazone) [18] and a potentially

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bidentate triazine 3-thione ligand [19], both derived from benzil and thiosemicarbazone, with mercury (II) nitrate and methylmercury chloride. In the three complexes characterized by X-ray diffraction, the ligands were only bonded to the mercury through the sulfur atom, giving a linear arrangement, results that point out the high affinity of mercury for the thiocarbonyl group and for a low coordination number.

In this paper we report the synthesis of the ligand benzaldehyde-N(4),N(4)-dimethylthiosemicarbazone LH and its complexes derived from the reaction with HgX_2 (X = Cl, Br, I or NO_3). We have obtained complexes with different Hg:LH ratio and with the ligand being neutral or deprotonated. The complexes have been characterized using NMR, IR and mass spectrometry. The X-ray single crystal structures of the complexes and the thiosemicarbazone LH are also reported.

2. Experimental

2.1. Physical measurements

Microanalyses were carried out using a LECO CHNS-932 Elemental Analyzer. IR spectra in the 4000–400 cm^{-1} range were recorded as KBr pellets on a Jasco FT/IR-410 spectrophotometer. Fast atom 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. Electrospray Ionization (ESI) mass spectra were performed with an ion trap instrument LCQ Deca XP plus (Thermo Instruments). An ESI source was used in positive ionization mode. The instrumental parameters were set as follows: mass range scanned from *m*/*z* 500 to 2000; Source Voltage (KV): 4.5; Seath gas flow rate: 11; Capillary Temperature (C): 250; Capillary Voltage (V): 38 and Tube Lens Voltage (V): 30. Conductivity data were measured using freshly prepared DMF solutions (ca. 10^{-3} M) at 25 °C with a Metrohm Herisau model E-518 instrument. ^1H and ^{13}C spectra were recorded on a spectrometer Bruker AMX-300 using $CDCl_3$ or DMSO-d_6 as solvents and TMS as internal reference.

2.2. Synthesis of the ligands and complexes

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

2.2.1. Preparation of benzaldehyde-N(4),N(4)-dimethylthiosemicarbazone, (*LH*)

The compound LH was prepared by condensation of benzaldehyde and N(4),N(4)-dimethylthiosemicarbazide. Benzaldehyde (0.5 mL, 4.9 mmol) was added over a solution of N(4),N(4)-dimethylthiosemicarbazide (0.500 g, 4.5 mmol) in ethanol:water 1:1 (15 mL). The yellow solution was stirred at room temperature for 3 h. The white solid formed was collected by filtration, washed thoroughly with distilled water, ethanol and diethyl ether and dried in vacuo. Yield 70%. *Anal.* Calc. 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) $[M+H]^+$. ^1H NMR ($CDCl_3$, δ ppm): 9.0 (s, 1H, NH), 7.7 (s, 1H, CH), 7.6 (m, 2H, Ph), 7.4 (m, 3H, Ph), 3.5 (s, 6H, CH_3). ^1H NMR ([D_6]DMSO, δ ppm): 10.9 (s, 1H, NH), 8.2 (s, 1H, CH), 7.6 (m, 2H, Ph), 7.4 (m, 3H, Ph), 3.2 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 181.8 (CS), 142.9 (CN), 134.1, 130.5, 129.2, 127.5 (Ph), 44.5 (CH_3). 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.

Single crystals suitable for X-ray diffraction analysis were obtained from the mother liquor.

2.2.2. Preparation of the complexes

*2.2.2.1. $[Hg(NO_3)(LH)_2]NO_3$ (**1**).* A solution of LH (0.100 g, 0.48 mmol) in ethanol (10 mL) was mixed with $Hg(NO_3)_2{\cdot}H_2O$ (0.082 g, 0.24 mmol). The mixture was stirred at room temperature for 2 h. The yellow precipitate was filtered off, washed with ethanol and diethyl ether and dried in vacuo. Yield 75%. MS (FAB): *m*/*z* (%): 614.9 (100) $[HgL(LH)]^+$. ^1H NMR ([D_6]DMSO, δ ppm): 9.0 (s, 1H, NH), 8.4 (d, 1H, CH), 7.8 (m, 2H, Ph), 7.5 (m, 3H, Ph), 3.2 (s, 6H, CH_3). ^{13}C NMR ([D_6]DMSO, δ ppm): 168.4 (CS), 153.0 (CN), 135.3, 132.7, 131.4, 129.3, 129.0, 128.4, 126.7, 125.6 (Ph), 41.4 (CH_3). IR (KBr, cm^{-1}): ν(NH) 3216, ν(CH) 3118, $\nu(CH)_{Ph}$ 3060, $\nu(CH)_{Me}$ 2931, $\nu(NO)_{NO3}$ 1768, 1698, 1537, ν(CN) 1603, δ(NCS) 1590, $\nu(NO)_{NO3}$ 1384,1315, ν(CS) 930.

Single crystals suitable for X-ray diffraction analysis were obtained from the mother liquor.

*2.2.2.2. $[Hg(L)_2]$ (**2**).* A solution of LH (0.100 g, 0.48 mmol) in ethanol (10 mL) with $LiOH{\cdot}H_2O$ (0.020 g, 0.48 mmol) was mixed with $Hg(NO_3)_2{\cdot}H_2O$ (0.082 g, 0.24 mmol). The mixture was stirred at room temperature for 4 h and the scarce solid was separated by filtration and discarded. A crystalline yellow solid was formed from evaporation of the filtrate overnight that was filtered off, washed with cold ethanol and diethyl ether and dried in vacuo. Yield 80%. (FAB): *m*/*z* (%): 614 (100) $[M+H]^+$. ^1H NMR ($CDCl_3$, δ ppm): 8.4 (s, 1H, CH), 8.2 (d, 1H, Ph), 7.5–7.2 (m, 4H, Ph), 3.2 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 153.1 (CS), 146.8 (CN), 134.0, 132.7, 131.4, 129.6, 129.2, 128.3. 128.1, 128.0 (Ph), 40.1, 39.6 (CH_3). IR (KBr, cm^{-1}): ν(CH) 3071, $\nu(CH)_{Ph}$ 3021, $\nu(CH)_{Me}$ 2920, δ(NCS) 1590, 1567, ν(CS) 877.

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the mother liquor.

This complex was also obtained from HgX_2 (Cl, Br or I) under the same reaction conditions.

*2.2.2.3. $[Hg(LH)_2(\mu\text{-}Cl)_2HgCl_2]$ (**3**).* A solution of LH (0.100 g, 0.48 mmol) in ethanol (10 mL) was mixed with $HgCl_2$ (0.132 g, 0.48 mmol). The mixture was stirred at room temperature for 4 h. The light yellow solid formed was filtered off, washed with ethanol and dried in vacuo. Yield 94%. (ESI): *m*/*z*: 614 $[HgL(LH)]^+$. ^1H NMR ([D_6]DMSO, δ ppm): 11.0 (s, 1H, NH), 8.4 (s, 1H, CH), 7.8 (m, 2H, Ph), 7.4 (m, 3H, Ph), 3.3 (s, 6H, CH_3). ^{13}C NMR ([D_6]DMSO, δ ppm): 174.5 (CS), 149.4 (CN), 133.6, 131.0, 129.6, 128.2 (Ph), 42.6 (CH_3). IR (KBr, cm^{-1}): ν(NH) 3192, ν(CH) 3121, $\nu(CH)_{Ph}$ 3055, 3022, $\nu(CH)_{Me}$ 2930, δ(NCS), 1602, 1577, ν(CS), 968.

This complex was also obtained working in a LH:HgX_2 2:1 molar ratio.

Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization in DMSO.

*2.2.2.4. $[Hg(LH)_2(\mu\text{-}Br)_2HgBr_2]$ (**4**).* The reaction was carried out using the procedure described above but using $HgBr_2$ (0.172 g, 0.48 mmol) instead of $HgCl_2$. Yield 90%. (ESI): *m*/*z*: 614 $[HgL(LH)]^+$. ^1H NMR ($CDCl_3$, δ ppm): 8.8 (s, 1H, NH), 7.6 (s, 1H, CH), 7.4 (m, 2H, Ph), 7.3 (m, 3H, Ph), 3.4 (s, 6H, CH_3). ^1H NMR ([D_6]DMSO, δ ppm): 8.4 (s, 1H, CH), 7.8 (m, 2H, Ph), 7.4 (m, 3H, Ph), 3.3 (s, 6H, CH_3). ^{13}C NMR ([D_6]DMSO, δ ppm): 173.2 (CS), 150.9 (CN), 133.2, 131.3, 129.2, 128.5 (Ph), 42.4 (CH_3). IR (KBr, cm^{-1}): ν(NH) 3195, ν(CH) 3138, $\nu(CH)_{Ph}$ 3061, 3000, $\nu(CH)_{Me}$ 2928, δ(NCS), 1601, 1580, ν(CS) 966.

This complex was also obtained working in a LH:HgX_2 2:1 molar ratio.

Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization in DMSO.

*2.2.2.5. $[HgI(LH)(\mu\text{-}I)_2HgI(LH)]$ (**5**) and $[HgI_2LH]$ (**6**).* The reaction was carried out following the procedure described for **3** but HgI_2

(0.220 g, 0.48 mmol) was used instead of $HgCl_2$. Data for the yellow solid formed (**5**): Yield 88%. (ESI): *m/z*: 535.9 $[HgI(LH)]^+$. ^1H NMR ([D_6]DMSO, δ ppm): 11 (s, 1H, NH), 8.5 (s, 1H, CH), 7.8 (m, 2H, Ph), 7.5 (m, 3H, Ph), 3.3 (s, 6H, CH_3). ^{13}C NMR ([D_6]DMSO, δ ppm): 173.4 (CS), 151.5 (CN), 133.0, 131.5, 129.2, 128.6 (Ph), 42.7 (CH_3). IR (KBr, cm^{-1}): ν(NH) 3279, ν(CH) 3138, $\nu(CH)_{Ph}$ 3061, 3015, $\nu(CH)_{Me}$ 2969, ν(CN) 1599, δ(HNCS) 1570, ν(CS) 959. Data for the light yellow crystalline material formed from the filtrate (**6**): Yield: 7%. (ESI): *m/z*: 535.9 $[HgI(LH)]^+$ ^1H NMR ($CDCl_3$, δ ppm): 9.1 (s, 1H, NH), 7.8 (s, 1H, CH), 7.6 (m, 2H, Ph), 7.4 (m, 3H, Ph), 3.4 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 171.8 (CS), 157.0 (CN), 131.3, 129.5, 128.8, 126.7(Ph), 41.5 (CH_3). IR (KBr, cm^{-1}): ν(NH) 3232, ν(CH) 3167, $\nu(CH)_{Ph}$ 3015, $\nu(CH)_{Me}$ 2925, δ(NCS), 1551, 1569, ν(CS) 953.

Complex **5** was also obtained working in a LH:HgX_2 2:1 molar ratio.

Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization in DMSO.

2.3. Crystallography

Single crystal X-ray diffraction measurement were performed using a Bruker AXS Kappa Apex-II diffractometer equipped with an Apex-II CCD area detector using a graphite monochromator (Mo Kα radiation, λ = 0.71073 Å). The substantial redundancy in data allows empirical absorption corrections (SADABS) [20] 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 [21].

The software package SHELXTL version 6.10 was used for space group determination, structure solution and refinement. The

Table 1
Crystallographic data for **LH** and complexes **1·H_2O**, **2** and **3**.

	LH	**1·H_2O**	**2**	**3**
Empirical formula	$C_{10}H_{13}N_3S$	$C_{20}H_{28}HgN_8O_7S_2$	$C_{20}H_{24}HgN_6S_2$	$C_{20}H_{26}Cl_4Hg_2N_6S_2$
Formula weight	207.29	757.21	613.16	957.57
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	*Pbca*	*P*2(1)/*c*	*P*2/*n*	*C*2/*c*
Unit cell dimensions	*a* = 13.225(3) Å α = 90°	*a* = 10.8557(9) Å α = 90°	*a* = 19.207(2) Å α = 90°	*a* = 19.1465(5) Å α = 90°
	b = 8.343(4) Å β = 90°	*b* = 18.7596(16) Å	*b* = 6.3971(6) Å	*b* = 11.2707(3) Å
	c = 18.993(6) Å γ = 90°	β = 104.360(3)°	β = 112.545(5)°	β = 125.1560(10)°
		c = 13.6196(12) Å γ = 90°	*c* = 19.215(2) Å γ = 90°	*c* = 16.0073(7) Å γ = 90°
Volume	2095.5(12) $Å^3$	2687.0(4) $Å^3$	2180.6(4) $Å^3$	2824.18(16) $Å^3$
Z	8	4	4	4
Density (calculated)	1.314 Mg/m^3	1.872 Mg/m^3	1.868 Mg/m^3	2.252 Mg/m^3
Absorption coefficient	0.273 mm^{-1}	5.939 mm^{-1}	7.269 mm^{-1}	11.407 mm^{-1}
F(0 0 0)	880	1488	1192	1792
Reflections collected	12 875	32 600	41 329	88 269
Independent reflections	2218 [R_{int} = 0.0960]	5883 [R_{int} = 0.0780]	4444 [R_{int} = 0.0694]	4343 [R_{int} = 0.0513]
Completeness to θ	95.2%	99.3%	99.8%	99.9%
Goodness-of-fit on F^2	1.002	1.120	1.037	1.142
Final R indices [$I > 2\sigma(I)$]	*R*1 = 0.0454, *wR*2 = 0.1036	*R*1 = 0.0414, *wR*2 = 0.0958	*R*1 = 0.0378, *wR*2 = 0.0985	*R*1 = 0.0210, *wR*2 = 0.0691
R indices (all data)	*R*1 = 0.0914, *wR*2 = 0.1238	*R*1 = 0.0765, *wR*2 = 0.1214	*R*1 = 0.0585, *wR*2 = 0.1171	*R*1 = 0.0302, *wR*2 = 0.0733
Largest difference in peak and hole	0.303 and −0.229 e.$Å^{-3}$	1.752 and −2.260 e.$Å^{-3}$	1.488 and −2.695 e.$Å^{-3}$	0.769 and −0.949 e.$Å^{-3}$

Table 2
Crystallographic data for complexes **4**, **5.2DMSO** and **6**.

Identification code	**4**	**5.2DMSO**	**6**
Empirical formula	$C_{20}H_{26}Br_4Hg_2N_6S_2$	$C_{24}H_{38}Hg_2I_4N_6O_2S_4$	$C_{10}H_{13}HgI_2N_3S$
Formula weight	1135.41	1479.62	661.68
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic	triclinic
Space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	*a* = 19.2278(8) Å α = 90°	*a* = 9.2624(5) Å α = 98.324(3)°	*a* = 7.7735(11) Å α = 89.794(10)°
	b = 11.5883(8) Å β = 126.045(5)°	*b* = 10.8890(7) Å β = 104.164(3)°	*b* = 10.3408(19) Å β = 71.431(7)°
	c = 16.2968(10) Å γ = 90°	*c* = 11.2364(7) Å γ = 112.903(3)°	*c* = 11.1497(16) Å γ = 67.953(7)°
Volume	2936.0(3) $Å^3$	974.98(10) $Å^3$	780.6(2) $Å^3$
Z	4	1	2
Density (calculated)	2.569 Mg/m^3	2.520 Mg/m^3	2.815 Mg/m^3
Absorption coefficient	16.053 mm^{-1}	11.275 mm^{-1}	13.931 mm^{-1}
F(0 0 0)	2080	676	592
Reflections collected	50 524	67 891	17 896
Independent reflections	4542 [R_{int} = 0.0732]	5014 [R_{int} = 0.0447]	3109 [R_{int} = 0.0510]
Completeness to θ	99.5%	99.5%	97.8%
Goodness-of-fit on F^2	1.029	1.194	1.085
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0477, *wR*2 = 0.1180	*R*1 = 0.0135, *wR*2 = 0.0321	*R*1 = 0.0241, *wR*2 = 0.0601
R indices (all data)	*R*1 = 0.0828, *wR*2 = 0.1373	*R*1 = 0.0148, *wR*2 = 0.0326	*R*1 = 0.0287, *wR*2 = 0.0637
Largest difference in peak and hole	3.518 and −3.808 e.$Å^{-3}$	0.564 and −0.852 e.$Å^{-3}$	2.170 and −1.265 e.$Å^{-3}$

structures were solved by direct methods (SHELXS-97) [22], 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 and conventional R factors (R) are based on F [23]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library. Experimental details of the X-ray structural analysis as well as the crystallographic data are summarized in Tables 1 and 2.

3. Results and discussion

3.1. Synthesis

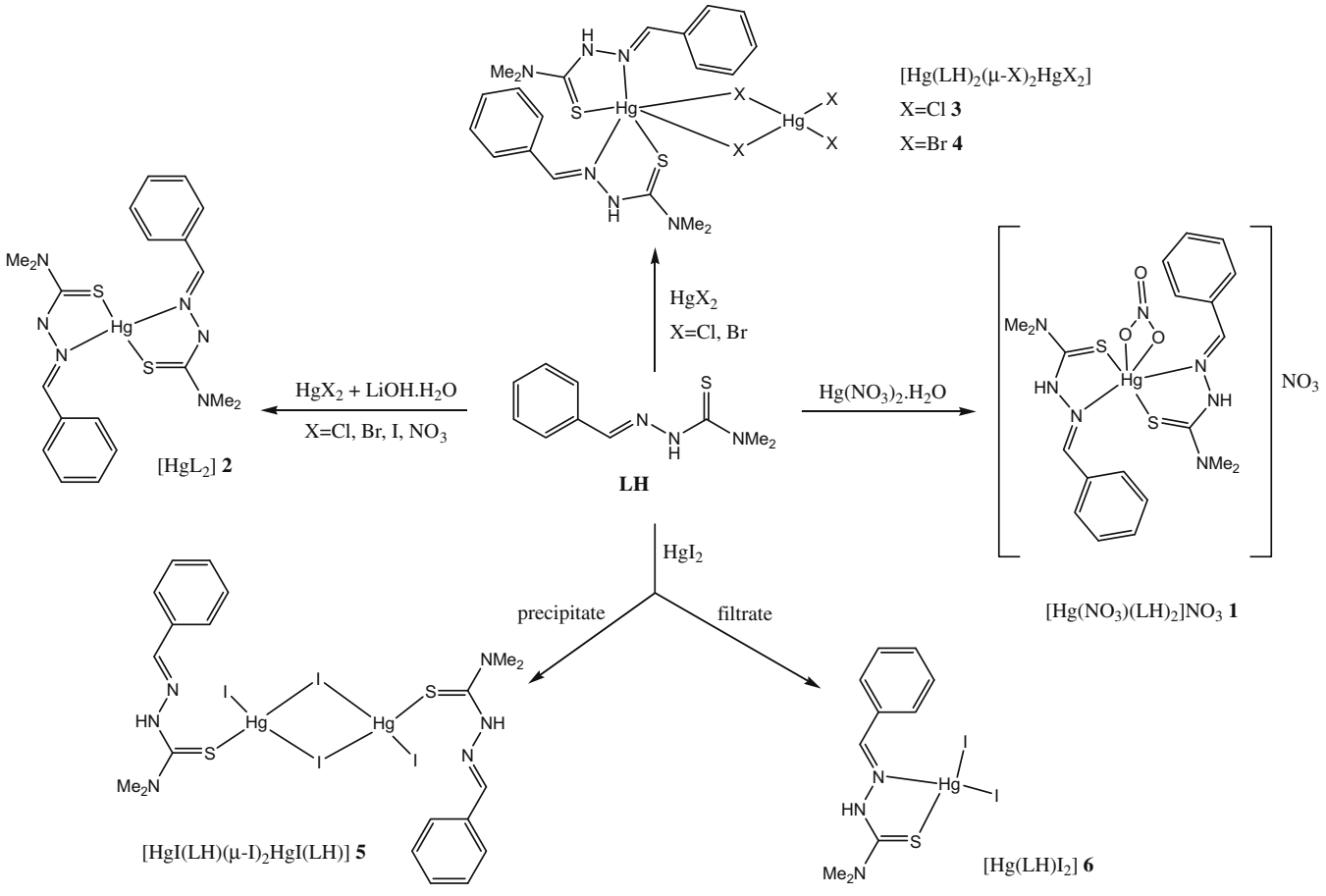
Benzaldehyde-N(4),N(4)-dimethylthiosemicarbazone, (**LH**) was prepared by condensation of benzaldehyde and N(4),N(4)-dimethylthiosemicarbazide in ethanol:water 1:1. The new molecule was unambiguously characterized by spectroscopic methods, as detailed in the Section 2, and by single crystal X-ray diffraction studies.

The synthesis of the complexes was carried out in ethanol, and in the case of complex **2**, also in the presence of the basic medium provided by $LiOH{\cdot}H_2O$ (Scheme 1). The structures of the complexes mainly depend on the counterion used. In the complexes the ligand behaves as a neutral molecule unless lithium hydroxide is used, which induces its deprotonation. Conductivity data indicate that the complexes are molecular species, except the nitrate derivative $[Hg(NO_3)(LH)_2]NO_3$ (**1**) [24]. The mass spectra of complexes **1**, **2**, **3** and **4** show a peak corresponding to $[Hg(L)(LH)]^+$ indicating a 1:2 Hg:LH ratio. In contrast, complexes **5** and **6** show the fragment $[HgI(LH)]^+$, corresponding to a 1:1 ratio.

3.2. Crystal structures

The structure determination of **LH** shows (Fig. 1) that in the solid state the thiosemicarbazone exists in the thione form, supported by the presence of hydrazinic hydrogens and a C–S distance of 1.678(3) Å, which is much shorter than a single C–S bond and where N(1) and S(1) are in a *cis* disposition. The ligand core is deviated from planarity, with a mean deviation of 0.79 Å for S(1) from the least-squares plane. The aromatic ring is forming a dihedral angle of 11.21° with this plane. The molecules form hydrogen bonds between the NH group and the sulfur atom [N(2)–H(2)···S(1)#1 3.431(3) Å, 165(83)° #1 $1-x+1/2, y+1/2, z$], forming infinite chains running parallel to the b axis. These chains are linked through S···S interactions (3.48 Å, sum of the Van der Waals radii 3.60 Å) along the a axis, leading a 2D network.

In all the complexes but **5** the N,S-coordination mode of the ligand affords one five-membered chelate ring. Coordination of mercury induces more electronic delocalization, which can be confirmed by the decrease in the C(2)–N(2) bond distance and the increase in the distance corresponding to the C–S groups observed in all the metal derivatives (Table 3). In complex **2** the ligand is in the thiol form, since deprotonation leads to the formation of a new C=N bond and the CS bond distance is close to the value expected for a single bond (Table 3). The Hg–S bonds are quite strong in all the complexes and are much shorter than the Hg–N bonds. In complexes **5** and **6** these bonds are the largest due to the presence of strong Hg–I bonds that weaken the Hg–S ones.



Scheme 1.

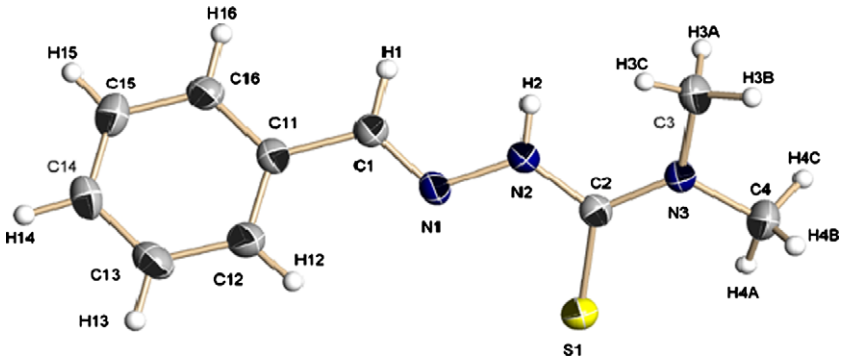


Fig. 1. Molecular structure of **LH** with 50% probability ellipsoids; bond lengths (Å): C(1)–N(1), 1.276(3); N(1)–N(2), 1.371(3); N(2)–C(2), 1.356(3); C(2)–N(3), 1.341(3); C(2)–S(1), 1.678(3); N(3)–C(3), 1.448(4); N(3)–C(4), 1.455(3); bond angles (°): C(1)–N(1)–N(2), 115.4(2); C(2)–N(2)–N(1), 120.5(2); N(3)–C(2)–N(2), 115.2(2); N(3)–C(2)–S(1), 122.58(18); N(2)–C(2)–S(1), 122.26(19).

Table 3
Selected bond distances (Å) of the ligand skeleton in LH and its complexes.

	LH	**1·H$_2$O**	**2**	**3**	**4**	**5**.2DMSO	**6**
C(1)–N(1)	1.276(3)	1.281(8)	1.285(9)	1.280(5)	1.262(11)	1.281(3)	1.273(7)
C(5)–N(4)		1.288(8)	1.296(9)				
N(1)–N(2)	1.371(3)	1.371(8)	1.377(8)	1.379(4)	1.384(9)	1.384(3)	1.385(6)
N(4)–N(5)		1.376(7)	1.357(8)				
N(2)–C(2)	1.356(3)	1.352(9)	1.294(9)	1.343(4)	1.342(10)	1.346(3)	1.343(6)
N(5)–C(6)		1.356(9)	1.327(9)				
C(2)–N(3)	1.341(3)	1.327(9)	1.363(11)	1.317(4)	1.321(10)	1.328(3)	1.327(7)
C(6)–N(6)		1.326(8)	1.349(9)				
C(2)–S(1)	1.678(3)	1.720(7)	1.769(8)	1.727(3)	1.711(8)	1.723(2)	1.713(5)
C(6)–S(2)		1.718(7)	1.768(8)				

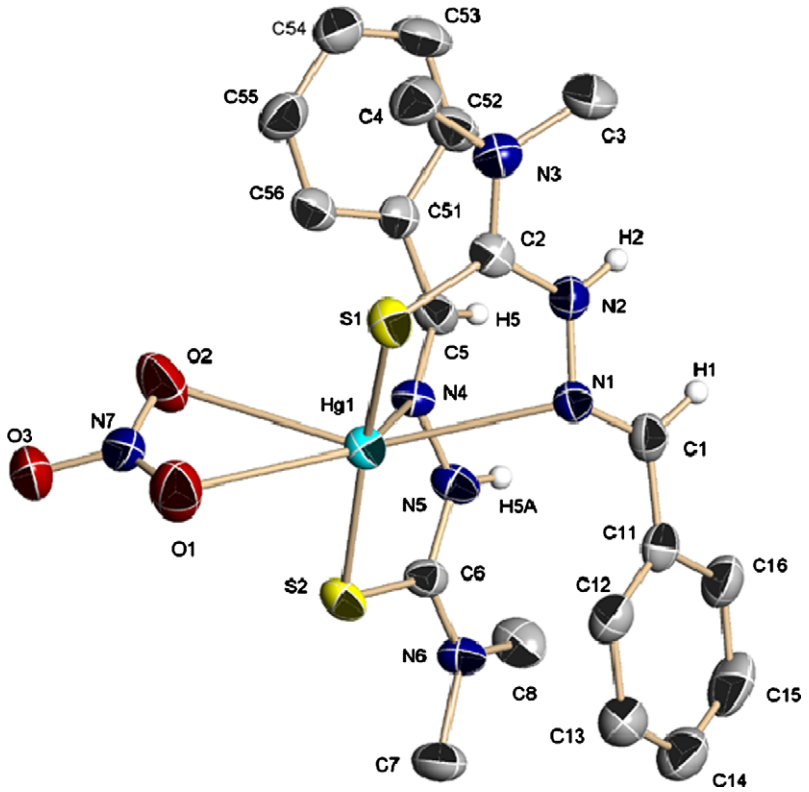


Fig. 2. Molecular structure of **1** with 50% probability ellipsoids, hydrogen atoms, the nitrate and the water molecule are omitted for clarity; bond lengths (Å): Hg(1)–S(1), 2.3576(18); Hg(1)–S(2), 2.3683(18); Hg(1)–N(4), 2.534(5); Hg(1)–N(1), 2.784(5); Hg(1)–O(2), 2.790(6); Hg(1)–O(1), 2.837(6); bond angles (°): S(1)–Hg(1)–S(2), 166.90(7); S(1)–Hg(1)–N(4), 116.60(13); S(2)–Hg(1)–N(4), 75.40(12); S(1)–Hg(1)–N(1), 70.44(11); S(2)–Hg(1)–N(1), 109.52(12); N(4)–Hg(1)–N(1), 76.52(17); S(1)–Hg(1)–O(2), 89.34(15); S(2)–Hg(1)–O(2), 95.25(15); N(4)–Hg(1)–O(2), 93.99(18); N(1)–Hg(1)–O(2), 149.78(17); S(1)–Hg(1)–O(1), 86.21(15); S(2)–Hg(1)–O(1), 88.49(14); N(4)–Hg(1)–O(1), 134.23(18); N(1)–Hg(1)–O(1), 148.55(18); O(2)–Hg(1)–O(1), 44.41(17).

The asymmetric unit of complex **1** contains one $[Hg(NO_3)(LH)_2]^+$ cation, one NO_3^- and a water molecule. In the cation, the mercury ion is bonded to two N,S-donor ligands and to a bidentate nitrato group in a strongly distorted octahedral arrangement, due to the small bite of the NO_3 ligand, with the sulfur atoms in the axial positions (Fig. 2). As far as we know, this complex represents the first example of a mercury complex crystallographically characterized containing a thiosemicarbazone ligand and a nitrato group. Within the ligands bond distances are very similar to those of free LH, although the backbone is more planar and the phenyl ring is more canted, since the angle that forms with the ligand skeleton is 22.50°. The phenyl groups are located on opposite sides, thus minimizing steric hindrance, which is observed in all the complexes containing two ligands bonded to the same mercury atom. In the literature there are few reports about crystalline structures of Hg compounds with bidentate nitrato ligands, and only two with a $N_2S_2O_2$ environment (any provided by nitrato), but the Hg–O bond distances falls within the range of other Hg–O bonds reported [25]. There is an extended network of hydrogen bonds involving the amine and nitrato groups, the nitrate anion and the water molecule (Table 4), leading a 3D architecture.

The asymmetric unit of complex **2** is formed by two crystallographically-distinct units of $[HgL_2]$, in which each metal ion is bonded to two deprotonated ligands in a bidentate mode, giving a N_2S_2 environment (Fig. 3). The τ_4 parameter is 0.57 and 0.55 for Hg(1) and Hg(2), respectively, so the geometry is intermediate between tetrahedral and square-planar ($\tau_4 = 0$ for SP and $\tau = 1$ for Td) [26]. Due to electronic delocalization after deprotonation, the ligand backbones are flat, with maximum deviations from the

Table 4
Hydrogen bonds for **1** [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(5)–H(5A)···O(6)	0.88	2.07	2.887(9)	154.1
N(2)–H(2)···O(7)	0.88	1.89	2.734(8)	160.5
O(7)–H(7D)···O(5)	0.89(2)	1.86(5)	2.623(13)	142(7)
O(7)–H(7E)···O(3)#1	0.90(2)	1.89(3)	2.785(9)	173(9)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y+1/2, -z+1/2$.

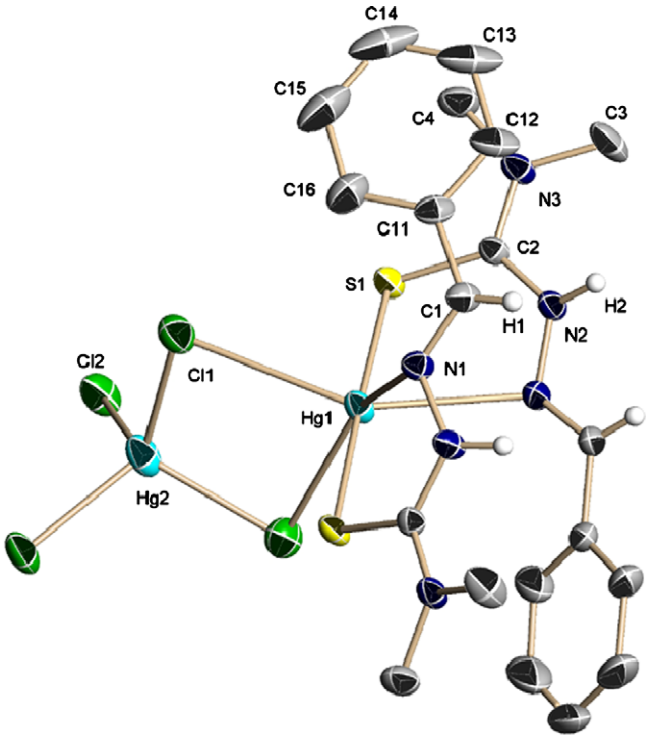


Fig. 4. Molecular structure of **3** with 50% probability ellipsoids, hydrogen atoms omitted for clarity. Data for **3**; bond lengths (Å): Hg(1)–S(1), 2.3732(8); Hg(1)–N(1), 2.748(3); Hg(1)–Cl(1), 3.0387(12); Hg(2)–Cl(2), 2.4653(10); Hg(2)–Cl(1), 2.4888(12); bond angles (°): S(1)#1–Hg(1)–S(1), 177.87(4); S(1)#1–Hg(1)–N(1), 71.54(6); S(1)–Hg(1)–N(1), 106.72(6); S(1)#1–Hg(1)–Cl(1), 102.20(3); S(1)–Hg(1)–Cl(1), 79.48(3); N(1)–Hg(1)–Cl(1). 109.65(7); Cl(2)#1–Hg(2)–Cl(2), 105.79(5); Cl(2)#1–Hg(2)–Cl(1), 114.50(4); Cl(2)–Hg(2)–Cl(1), 110.65(4); Cl(1)#1–Hg(2)–Cl(1), 101.01(6); Hg(2)–Cl(1)–Hg(1), 90.29(4). Data for **4**; bond lengths (Å): Hg(1)–S(1), 2.3819(19); Hg(1)–N(1), 2.764(7); Hg(1)–Br(1), 3.1317(10); Hg(2)–Br(2), 2.5788(9); Hg(2)–Br(1), 2.6204(10); bond angles (°): S(1)#1–Hg(1)–S(1), 177.82(10); S(1)#1–Hg(1)–N(1), 106.98(14); S(1)–Hg(1)–N(1), 71.22(14); S(1)#1–Hg(1)–Br(1), 102.00(5); S(1)–Hg(1)–Br(1), 79.68(5); N(1)–Hg(1)–Br(1), 150.54(13); N(1)–Hg(1)–Br(1)#1, 108.59(14); Br(1)–Hg(1)–Br(1)#1, 81.51(4); Br(2)#1–Hg(2)–Br(2), 107.22(5); Br(2)#1–Hg(2)–Br(1)#1, 110.60(3); Br(2)–Hg(2)–Br(1)#1, 112.98(3); Br(2)–Hg(2)–Br(1), 110.60(3); Br(1)#1–Hg(2)–Br(1), 102.56(5), Hg(2)–Br(1)–Hg(1), 87.97(3). Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$.

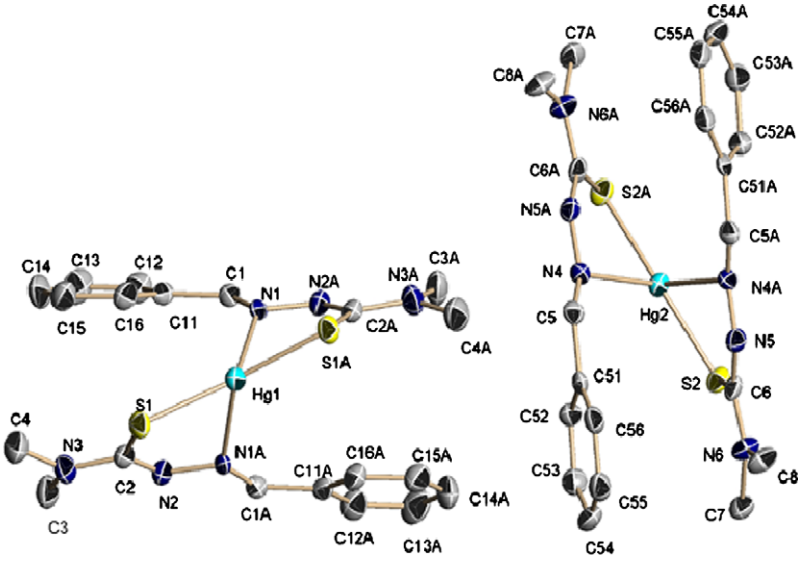


Fig. 3. Molecular structure of **2** with 50% probability ellipsoids, hydrogen atoms omitted for clarity; bond lengths (Å): S(2)–Hg(2), 2.3570(17); S(1)–Hg(1), 2.3612(19); Hg(2)–N(4), 2.537(6); Hg(1)–N(1), 2.532(6); bond angles (°): S(2)–Hg(2)–S(2)#1, 163.83(10); S(2)–Hg(2)–N(4), 118.98(13); S(2)#1–Hg(2)–N(4), 74.34(13); N(4)–Hg(2)–N(4)#1, 80.6(3); S(1)#2–Hg(1)–S(1), 156.00(10); S(1)–Hg(1)–N(1)#2, 76.18(13); S(1)–Hg(1)–N(1), 123.74(13); N(1)#2–Hg(1)–N(1), 80.8(3). Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, y, -z+1/2$ #2 $-x+3/2, y, -z+1/2$.

least-squares planes of −0.069 Å for N(2) and −0.026 Å for N(6). The phenyl ring is canted 14.19° in the unit containing Hg(1) and 29.89° in the unit containing Hg(2).

Complexes **3** and **4** are isomorphous, having the same structure, so they will be discussed together and only pictures corresponding to **3** will be depicted. Both complexes consist of HgX_4^{2-} units with two of the X^- ligands acting as bridges to link the $[Hg(LH)_2]^{2+}$ moieties (Fig. 4). This leads to one mercury ion with $N_2S_2X_2$ environment in a distorted octahedral arrangement and to another metal with a X_4 coordination in a tetrahedral disposition (τ_4 is 0.96 for complex **3** and 0.97 for complex **4**). The ligands can be considered planar, with maximum deviations from the least-squares planes of 0.081 Å for C(2) in complex **3** and 0.069 Å for N(1) in complex **4**. The phenyl rings form dihedral angles of 29.73° and 27.93° in complexes **3** and **4**, respectively. The halogen bridges are quite asymmetric, with one bond distance much longer than the other, although the largest are within the range of other complexes found in the literature [27–29]. The molecules are held together by hydrogen bonds between the terminal halogen groups and the amine groups forming infinite chains running along *b* [N(2)–H(2)···Cl(2)#2 3.286(3) Å, 168(5)°; N(2)–H(2)···Br(2)#2 3.492(7) Å, 169(6)° #2 *x*, *y*−1, *z*].

The asymmetric unit of complex **5** recrystallized in DMSO contains one molecule of the complex and two of DMSO. The [HgI(LH)(μ-I)$_2$HgI(LH)] units are centrosymmetric with the inversion point located in the middle of the Hg–Hg distance. Each mercury atom has a SI_3 coordination, provided by one neutral S-bonded ligand, one terminal iodido and two iodido bridges, giving a distorted tetrahedral geometry, with τ_4 = 0.82 (Fig. 5). The ligand, including the phenyl ring, lies almost in the same plane (dihedral angle 4.27°). The iodido bridges, as well as occurs with Cl and Br, are quite asymmetric, but the distances are within the range found in related structures [30,31]. The DMSO molecules are linked by hydrogen bonds with the amine groups [N(2)–H(2)···O(1)#2 2.857(3) Å, 152.6°, #2 *x*−1, *y*, *z*−1], and short I(2)···I(2) contacts, 3.86 Å, form infinite chains along the *b* axis.

The molecular structure of complex **6** is formed by one mercury ion bonded to one neutral ligand through the imine nitrogen and the sulfur atom and to two iodidos (Fig. 6), giving rise to a NSI_2 environment in a distorted tetrahedral geometry (τ_4 = 0.80). The ligand can be considered planar being the maximum deviation from the least-squares plane of 0.0661 Å for N(2), and with the phenyl ring forming a dihedral angle of 17.64°. The molecules are forming dimers through hydrogen bonds between I(1) and the amine group [N(2)–H(2)···I(1)#1 3.977(5) Å, 162.0°, #1 −*x*+1, −*y*+1, −*z*]. These dimers are linked by I(2)···I(2) contacts with a distance of 2.93 Å, and I(1)···I(1) with a distance of 3.88 Å, which are slightly shorter than the sum of the Van der Waals radii, 3.96 Å, giving rise to a 2D structure in the *ac* plane.

3.3. Infrared spectra

The band corresponding to ν(N–H) is observed, except in complex **2**, indicating that the ligand behaves as a neutral molecule, but is deprotonated in complex **2**. The coordination by sulfur induces the band at 1020 cm^{-1} is shifted to lower frequency. All the spectra show a band assigned to the ν(C–H), which is clearly shifted in complex **2**, in which the ligand has lost the acidic hydro-

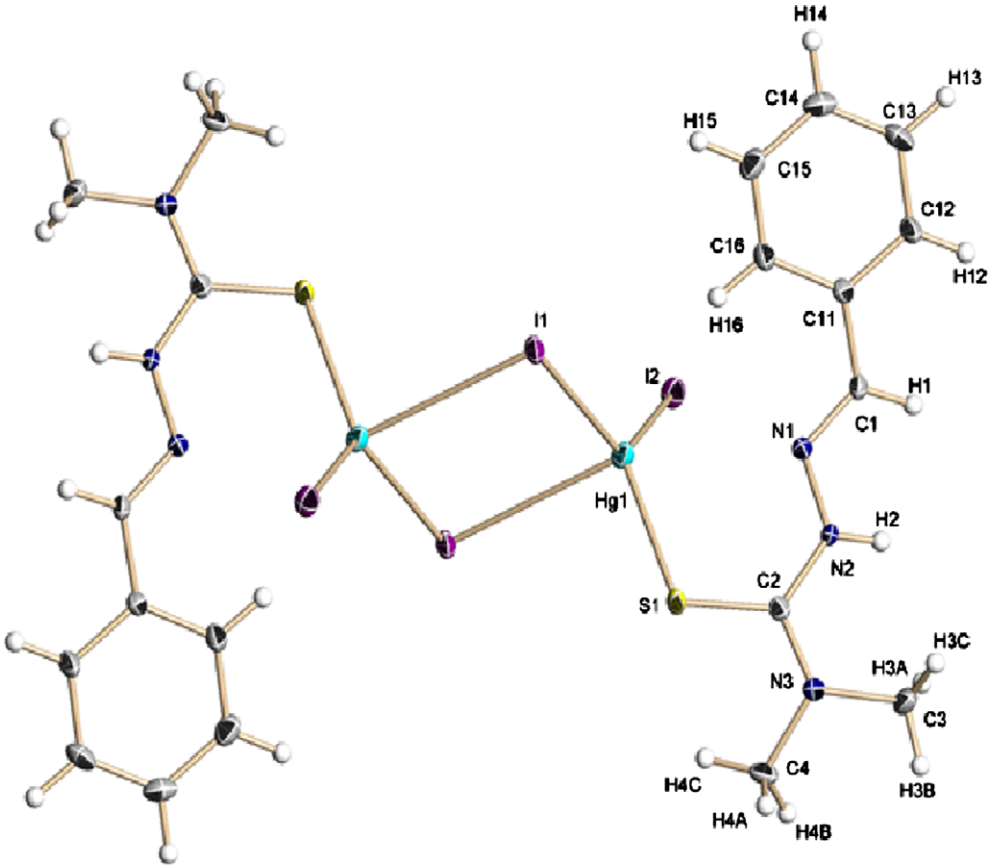


Fig. 5. Molecular structure of **5** with 50% probability ellipsoids; bond lengths (Å): Hg(1)–S(1), 2.4863(6); Hg(1)–I(2), 2.6751(2); Hg(1)–I(1), 2.7535(2); Hg(1)–I(1)#1, 3.2297(2); bond angles (°): S(1)–Hg(1)–I(2), 122.094(15); S(1)–Hg(1)–I(1), 114.274(16); I(2)–Hg(1)–I(1), 122.623(7); S(1)–Hg(1)–I(1)#1, 93.148(15); I(2)–Hg(1)–I(1)#1, 98.111(6); I(1)–Hg(1)–I(1)#1, 88.342(6); Hg(1)–I(1)–Hg(1)#1, 91.658(6). Symmetry transformations used to generate equivalent atoms: #1 −*x*, −*y*, −*z*+1.

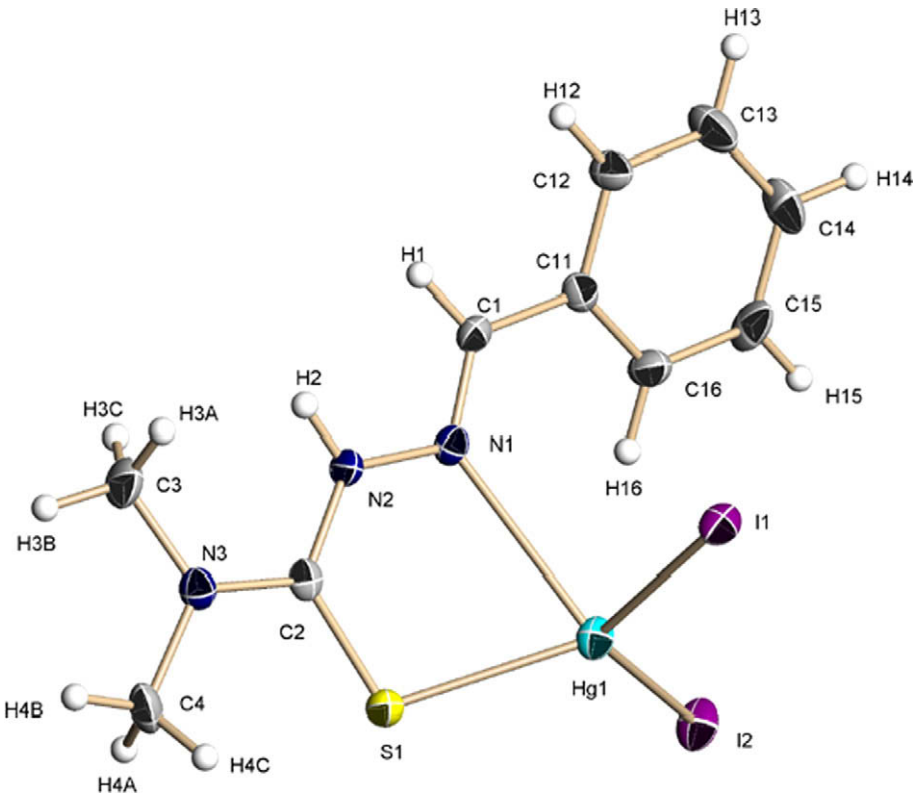


Fig. 6. Molecular structure of **6** with 50% probability ellipsoids; bond lengths (Å): Hg(1)–S(1), 2.4926(14); Hg(1)–I(2), 2.6764(5); Hg(1)–I(1), 2.6853(5); Hg(1)–N(1), 2.687(4); bond angles (°): S(1)–Hg(1)–I(2), 112.73(4); S(1)–Hg(1)–I(1), 123.83(4); I(2)–Hg(1)–I(1), 122.488(16); S(1)–Hg(1)–N(1), 72.06(9); I(2)–Hg(1)–N(1), 116.81(9); I(1)–Hg(1)–N(1), 90.98(9).

gen atom. The spectrum of complex **1** shows several bands corresponding to nitrate and nitrato groups, which support the presence of NO_3^- acting both as ligand and counterion.

3.4. NMR spectra

The new compounds were also characterized by NMR spectroscopy. The spectrum of the ligand displays well-resolved ^1H NMR signals, which correlate well with the hydrogen atoms present in the molecule. The ^{13}C NMR spectrum of LH also show the signals corresponding to the carbon atoms expected for the condensation product between benzaldehyde and N(4),N(4)-dimethylthiosemicarbazide.

In the ^1H NMR ($CDCl_3$) spectrum of complex **2**, the absence of the N–H signal is consistent with the thiosemicarbazone being deprotonated. The ^1H NMR spectra of the rest of the complexes confirm that the ligand is in its neutral form. Spectrum of complex **4** in [D_6]DMSO, does not show the signal corresponding to the NH proton, although it is observed in $CDCl_3$. In the ^{13}C NMR spectra, the signals corresponding to the imine carbons and the thiocarbonyl groups are clearly shifted on complexation.

4. Conclusions

The reactions were carried out in ethanol and the behavior of the ligand, as monoanion or as a neutral molecule, only depends on the presence or the absence of lithium hydroxide. On the other hand, the ligand:mercury ratio in the complexes does not depend on the stoichiometry used in the reaction and their structures are only determined by the counterion used. Thus from nitrate a 1:2 complex was obtained, while from chloride, bromide or iodide, all the complexes show a 1:1 ratio. Complexes **1**, **2** and **6** are monomers, but complexes **3**, **4** and **5** show a dinuclear structure. Compounds **3** and **4** contain two different mercury ions: one has a $N_2S_2X_2$ coordination sphere that has not been observed to date in any crystal structure reported, while the other one is bonded to four halide ions. In contrast, in complex **5** both mercury atoms have a SI_3 coordination, since the ligand is only bonded through the sulfur atom.

Complexes **3** and **4**, consisting in dinuclear species containing two mercury atoms with different coordination environments, one octahedral and one tetrahedral, are scarce and represents the first example of this kind of compounds with a thiosemicarbazone ligand.

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Appendix A. Supplementary material

CCDC 733645, 733646, 733647, 733648, 733649, 733650 and 733651 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5**, **6** and **LH**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.08.029.

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