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Schiff bases derived from mercury(II)–aminothiolate complexes as metalloligands for transition metals

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Abstract

Mercury(II) complexes of aromatic aminothiolate ligands of formula [Hg(n-SC$_6$H$_4$NH$_2$)$_2$], $n = 3$ (**1**) or 4 (**2**) and [RHg(n-SC$_6$H$_4$NH$_2$)], R = Me, $n = 3$ (**3**) or 4 (**4**); R = Ph, $n = 3$ (**5**) or 4 (**6**) have been obtained and characterized by infrared and ^{1}H, ^{13}C and ^{199}Hg-NMR spectroscopies. The latter indicates that, in solution, complexes **1**–**6** have an essentially linear coordination about Hg(II). Unprecedented Schiff bases containing the Hg–S(thiolate) bond have been synthesized from **3**–**6** and salicylaldehyde yielding complexes of formula [RHg(n-SC$_6$H$_4$N=CHC$_6$H$_4$OH)], R = Me, $n = 3$ (**7**) or 4 (**8**); R = Ph, $n = 3$ (**9**) or 4 (**10**). The template reaction of **3** and **4** with M(CH$_3$COO)$_2$, M = Zn(II), Cd(II), and salicylaldehyde has afforded trimetallic complexes of formula [M^{II}\{MeHg(n-SC$_6$H$_4$N=CHC$_6$H$_4$O)\}$_2$], M = Zn, $n = 3$ (**11**) or 4 (**12**); M = Cd, $n = 3$ (**13**) or 4 (**14**). Complexes **7**–**14** have also been explored by use of infrared and NMR spectroscopies. The crystal structure determination of **2**, **3**, **5**, **7** and **8** by X-ray diffraction shows that Hg(II) has an essentially linear coordination. The presence of additional secondary Hg···S interactions in all these complexes leads to an increase in the coordination number of Hg to 4 or 5. In **2**, the interaction of each S–Hg–S unit with three neighbouring units gives rise to a polymeric chain, which can be considered as being formed by pairs of fused incomplete cubanes. In **3**, **5**, **7** and **8**, secondary Hg···S bonds between pairs of C–Hg–S fragments yield Hg$_2$S$_2$ dimers. In **3**, these dimers afford two-dimensional sheets by means of additional Hg···N secondary interactions. The crystal packing of the Hg$_2$S$_2$ dimers in **5**, **7** and **8** is very similar and gives rise to one-dimensional chains by means of additional Hg···S bonds. The resulting polymeric zig-zag ladders can be described as formed by Hg$_4$S$_4$ pseudo-cubanes sharing opposite faces.

Keywords: Mercury complexes; Aminothiolate ligands; Schiff base; X-ray crystallography; NMR spectroscopy

1. Introduction

Mercury–thiolate complexes are well known for their unusual coordination environments and provide an outstanding example of the structural diversity found in the wide family of metal thiolates [1]. Thus, the occurrence of two-, three- and four-coordination geometries, the presence of secondary mercury–sulfur interactions and the range in size from discrete species to polymeric structures are remarkable features, now well established but difficult to predict, in the chemistry of Hg(II) thiolates [2]. With the aim of contributing to the study of the main factors affecting their final structure, we obtained and structurally characterized several Hg(II) complexes with aliphatic aminothiol ligands, which under appropriate conditions behave as monofunctional thiols with a solubilizing amino group [3–7]. However, not only does the question of what determines the stereochemistry around mercury remain as yet unresolved, but also evaluation of the possible answer seems rather intricate. As an example, two different mercury complexes in both mononuclear and polymeric forms, with linear and tetrahedral coordination, respectively, were obtained with 3-dimethylamino-1-propanethiol ligand from apparently identical synthetic procedures [8].

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In order to extend the current knowledge of the chemistry of Hg(II) thiolates, we have undertaken the synthesis and structural characterization of the complexes obtained with Hg(II) and several aromatic aminothiol ligands. The existence of an uncoordinated amino group in the previous complexes has allowed for further modification of the coordinated ligand by means of condensation with the carbonyl group of salicylaldehyde and subsequent formation of a Schiff base. This, in turn, can behave as a metalloligand towards different metal centres. All these results, together with the crystal structure of five of these complexes are reported below.

2. Experimental

2.1. General

Only the preparations of complexes of formula $[Hg(n\text{-}SC_6H_4NH_2)_2]$, $n = 3$ (**1**) or 4 (**2**) were carried out by standard Schlenk techniques under a nitrogen atmosphere. The organic solvents were dried by conventional methods when used in the reactions carried out in non-aqueous media. Commercial 3-aminothiophenol, 4-aminothiophenol and salicylaldehyde from Aldrich, $M(CH_3COO)_2$ for M = Zn, Cd or Hg (Fluka), MeHgCl (Alfa Aesar) and $PhHgOOCCH_3$ (Fluka) were used as supplied. MeHgOH was obtained in situ from MeHgCl and Ag_2O. Microanalyses were performed with a Carlo Erba NA-1500 analyser. Infrared spectra were recorded from KBr discs on a Perkin–Elmer 1710 spectrometer for the range 4000–400 cm^{-1}. ^1H and ^{13}C-NMR spectra were run from DMSO-d_6 solutions on Bruker AC 250 or AM 400 spectrometers using tetramethylsilane as internal standard for ^1H and ^{13}C chemical shifts. The ^{199}Hg-NMR spectra were recorded from 0.1 M solutions in DMSO-d_6, in a Bruker AM 400 spectrometer using HgI_2 as external standard. The conversion of the ^{199}Hg chemical shifts to the more common $HgMe_2$ reference is $\delta(HgMe_2, \text{ext}) = \delta(HgI_2, \text{ext}; 1\ M/DMSO) - 3106$ ppm [9].

2.2. Preparation of the complexes

2.2.1. Synthesis of $[Hg(3\text{-}SC_6H_4NH_2)_2]$ (1)

The $3\text{-}HSC_6H_4NH_2$ ligand (0.32 ml, 3 mmol) was slowly added to a suspension of $Hg(CH_3COO)_2$ (0.478 g, 1.5 mmol) in 40 ml of acetonitrile and the mixture stirred for 15 min to give a light green solid. The precipitate was collected by filtration, washed with acetonitrile and diethyl ether. Yield, 0.538 g (79.9%). Anal. Calc. for $C_{12}H_{12}HgN_2S_2$: C 32.11; H 2.67; N 6.24; S 14.29. Found: C 32.02; H 2.67; N 6.19; S 13.99%. IR (cm^{-1}) 3491 and 3408 ν(N–H); 1626 and 1594 δ(N–H).

2.2.2. Synthesis of $[Hg(4\text{-}SC_6H_4NH_2)_2]$ (2)

This complex was obtained by a procedure analogous to that used for **1**. Light green solid was obtained, 0.857 g (93.2%). Anal. Calc. for $C_{12}H_{12}HgN_2S_2$: C 32.11; H 2.67; N 6.24; S 14.29. Found: C 32.04; H 2.63; N 6.24; S 14.42%. IR (cm^{-1}) 3384 and 3354 ν(N–H); 1619 and 1595 δ(N–H). Yellow laminar crystals were grown from CH_3CN solution.

2.2.3. Synthesis of $[MeHg(3\text{-}SC_6H_4NH_2)_2]$ (3)

An excess of freshly prepared Ag_2O was slowly added to a suspension of MeHgCl (1.057 g, 4 mmol) in 250 ml of water. The reaction mixture was allowed to stir for 24 h, at which time the AgCl formed and the unreacted Ag_2O were separated by filtration. Then, the $3\text{-}HSC_6H_4NH_2$ ligand (0.425 ml, 4 mmol) was slowly added to the previous filtrate containing CH_3HgOH. The resulting yellow solution was stirred for 12 h, at which time the oil formed on the walls of the reaction flask was separated from the solution and treated with diethylether to give a white solid, 0.996 g (73.30%). Anal. Calc. for C_7H_9HgNS: C 24.75; H 2.65; N 4.12; S 9.44. Found: C 24.82; H 2.41; N 4.21; S 9.28%. IR (cm^{-1}) 3399 and 3312 ν(N–H); 1610 and 1582 δ(N–H). Colourless block-shaped crystals were formed in $CHCl_3$ solution.

2.2.4. Synthesis of $[MeHg(4\text{-}SC_6H_4NH_2)_2]$ (4)

A solution of $4\text{-}SC_6H_4NH_2$ (0.417 ml, 3 mmol) in 10 ml of methanol was slowly added to an aqueous solution containing MeHgOH. This was prepared according to the procedure described above from MeHgCl (0.793 g, 3 mmol) in 250 ml of water and Ag_2O in excess. The reaction mixture was allowed to stir for 24 h and the resulting solid formed was separated by filtration and washed with 10–20 ml of methanol. Addition of this methanol to the filtrate afforded a second crop of solid. Both showed coincident elemental analyses. Total yield 0.996 g (73.30%). Anal. Calc. for C_7H_9HgNS: C 24.75; H 2.65; N 4.12; S 9.44. Found: C 24.94; H 2.58; N 4.13; S 9.44%. IR (cm^{-1}) 3419 and 3335 ν(N–H); 1617 and 1594 δ(N–H).

2.2.5. Synthesis of $[PhHg(3\text{-}SC_6H_4NH_2)_2]$ (5)

The $3\text{-}SC_6H_4NH_2$ ligand (0.212 g, 2 mmol) was slowly added to a suspension of $PhHgOOCCH_3$ (0.673 g, 2 mmol) in 80 ml of methanol. The reaction mixture was allowed to stir for 24 h, at which time it was concentrated and the solid filtered off and washed with diethylether. Yield, 0.591 g, 73.51%. Anal. Calc. for $C_{12}H_{11}HgNS$: C 35.87; H 2.74; N 3.49; S 7.98. Found: C 35.51; H 2.62; N 3.49; S 8.16%. IR (cm^{-1}) 3402 and 3313 ν(N–H); 1619 and 1585 δ(N–H). Single crystals were obtained from CH_2Cl_2 solution containing a few drops of isopropanol.

2.2.6. Synthesis of [PhHg(4-SC$_6$H$_4$NH$_2$)$_2$] (**6**)

A solution of 4-SC$_6$H$_4$NH$_2$ (0.649 g, 4.7 mmol) in 10 ml of methanol was slowly added to a suspension of PhHgOOCCH$_3$ (1.570 g, 4.7 mmol) in 40 ml of methanol. The reaction mixture was allowed to stir for 24 h, at which time the resulting solid formed was filtered off and washed with methanol. Yield, 1.430 g, 76.30%. Anal. Calc. for $C_{12}H_{11}HgNS$: C 35.87; H 2.74; N 3.49; S 7.98. Found: C 35.62; H 2.67; N 3.52; S 8.02%. IR (cm^{-1}) 3462 and 3372 ν(N–H); 1614 and 1595 δ(N–H).

2.2.7. Synthesis of [MeHg(3-SC$_6$H$_4$N=CHC$_6$H$_4$OH)] (**7**)

A mixture of **3** (0.353 g, 1.04 mmol) and salicylaldehyde (109.4 μl, 1.04 mmol) in 60 ml of toluene containing a small amount of *p*-toluenesulfonic acid in order to catalyse the condensation reaction was added to a reaction flask equipped with a mini Dean–Stark trap. The final solution was refluxed for 3 h under a nitrogen atmosphere, while the reaction was monitored by thin layer chromatography. At this time solid NaHCO$_3$ was added in order to neutralize the remaining *p*-toluenesulfonic acid. The sodium salt thus formed and the excess of NaHCO$_3$ were separated by filtration and the filtrate evaporated to dryness. The oily residue was treated successively with diethyl ether, affording a pale yellow solid. Yield, 0.134 g, 29.1%. Anal. Calc. for $C_{14}H_{13}HgNOS$: C 37.98; H 2.93; N 3.16; S 7.22. Found: C 37.52; H 2.94; N 3.09; S 7.10%. IR (cm^{-1}) 2908 ν(C–H), 1618 ν(C=N) and 1280 ν(C–O). Yellow needles were obtained from a CHCl$_3$–C$_6$H$_6$ solution.

2.2.8. Synthesis of [MeHg(4-SC$_6$H$_4$N=CHC$_6$H$_4$OH)] (**8**)

A similar procedure to that described for **7** was followed. Thus, a solution of **4** (0.401 g, 1.8 mmol) and salicylaldehyde (124.3 μl, 1.8 mmol) in 80 ml of toluene containing a small amount of *p*-toluenesulfonic acid was refluxed for 24 h. The final solid residue was dried with diethyl ether, affording an orange solid. Yield, 0.359 g, 68.5%. Anal. Calc. for $C_{14}H_{13}HgNOS$: C 37.98; H 2.93; N 3.16; S 7.22. Found: C 37.94; H 3.00; N 3.09; S 7.07%. IR (cm^{-1}) 2905 ν(C–H), 1615 ν(C=N) and 1283 ν(C–O). Single crystals were grown by slow evaporation from acetone solution.

2.2.9. Synthesis of [PhHg(3-SC$_6$H$_4$N=CHC$_6$H$_4$OH)] (**9**)

The synthetic procedure is analogous to that of **7**. In this case, a solution of **5** (0.381 g, 0.95 mmol) and salicylaldehyde (99.8 μl, 0.95 mmol) was refluxed in 70 ml of toluene for 8 h, affording a pale yellow solid. Yield, 0.368 g, 76.7%. Anal. Calc. for $C_{19}H_{15}HgNOS$: C 45.11; H 2.97; N 2.77; S 6.34. Found: C 45.34; H 3.00; N 2.69; S 6.07%. IR (cm^{-1}) 3045 ν(C–H), 1624 ν(C=N) and 1281 ν(C–O).

2.2.10. Synthesis of [PhHg(4-SC$_6$H$_4$N=CHC$_6$H$_4$OH)] (**10**)

The synthetic procedure is essentially the same as that of **7**. In this case, the suspension of **6** (0.418 g, 1.04 mmol) in 80 ml of toluene was kept under reflux until complete dissolution and then salicylaldehyde (109.5 μl, 1.04 mmol) was added. The reflux was kept for 24 h, and the reaction afforded a pale yellow solid. Yield, 0.227 g, 43.13%. Anal. Calc. for $C_{19}H_{15}HgNOS$: C 45.11; H 2.97; N 2.77; S 6.34. Found: C 45.52; H 3.06; N 2.61; S 6.25%. IR (cm^{-1}) 3044 ν(C–H), 1611 ν(C=N) and 1277 ν(C–O).

2.2.11. Synthesis of [Zn{MeHg(3-SC$_6$H$_4$N=CHC$_6$H$_4$O)}$_2$] (**11**)

A solution of Zn(CH$_3$COO)$_2$·2H$_2$O (0.088 g, 0.40 mmol) in 25 ml of absolute ethanol was slowly added with stirring to the pale yellow solution containing **3** (0.289 g, 0.85 mmol) and salicylaldehyde (84.2 μl, 0.80 mmol) in 50 ml of the same solvent. The resultant clear yellow solution was refluxed for 3 h, at which time the thin layer chromatography indicated that the initial complex **3** had totally reacted. Concentration of the solution to half of its initial volume afforded a yellow solid. Yield, 0.206 g, 54.1%. Anal. Calc. for $C_{28}H_{24}Hg_2N_2O_2S_2Zn$: C 35.36; H 2.54; N 2.95; S 6.74. Found: C 35.45; H 2.75; N 2.95; S 6.56%. IR (cm^{-1}) 2907 ν(C–H), 1610 ν(C=N), 1541 and 1311 ν(C–O).

2.2.12. Synthesis of [Zn{MeHg(4-SC$_6$H$_4$N=CHC$_6$H$_4$O)}$_2$] (**12**)

The synthetic procedure is analogous to that followed for **11**. However, in this case, the addition of Zn(CH$_3$COO)$_2$·2H$_2$O (0.088 g, 0.40 mmol) in 20 ml of absolute ethanol to the yellow solution containing **4** (0.289 g, 0.85 mmol) and salicylaldehyde (84.2 μl, 0.80 mmol) in 40 ml of the same solvent gave rise to the formation of a precipitate, which became soluble when the mixture was heated. The reaction was completed after 1 h of reflux. Concentration of the solution to 10 ml afforded a yellow solid. Yield, 0.217 g, 57.0%. Anal. Calc. for $C_{28}H_{24}Hg_2N_2O_2S_2Zn$: C 35.36; H 2.54; N 2.95; S 6.74. Found: C 35.28; H 2.68; N 2.97; S 6.73%. IR (cm^{-1}) 2908 ν(C–H), 1602 ν(C=N), 1532 and 1327 ν(C–O).

2.2.13. Synthesis of [Cd{MeHg(3-SC$_6$H$_4$N=CHC$_6$H$_4$O)}$_2$] (**13**)

The synthetic procedure is analogous to that followed for **11**. Thus, a solution of Cd(CH$_3$COO)$_2$·2H$_2$O (0.080 g, 0.30 mmol) in 10 ml of absolute ethanol was added to the pale yellow solution containing **3** (0.221 g, 0.65 mmol) and salicylaldehyde (63.2 μl, 0.60 mmol) in 70 ml of the same solvent. A precipitate appeared after 30 min of reflux, which was maintained for 12 h. Filtration of the warm solution afforded a yellow solid.

Yield, 0.126 g, 42.1%. Anal. Calc. for $C_{28}H_{24}CdHg_2N_2O_2S_2\cdot\frac{1}{2}EtOH$: C 33.69; H 2.81; N 2.42; S 6.42. Found: C 34.11; H 2.64; N 2.74; S 6.28%. IR (cm^{-1}) 2906 ν(C–H), 1611 ν(C=N), 1541 and 1312 ν(C–O).

2.2.14. Synthesis of [Cd{MeHg(4-$SC_6H_4N{=}CHC_6H_4OH$)}$_2$] (**14**)

The synthetic procedure is analogous to that followed for **11**. Thus, a solution of $Cd(CH_3COO)_2\cdot 2H_2O$ (0.080 g, 0.30 mmol) in 10 ml of absolute ethanol was added to the pale yellow solution containing **4** (0.221 g, 0.65 mmol) and salicylaldehyde (63.2 μl, 0.60 mmol) in 40 ml of the same solvent. A yellow precipitate appeared after 2 h of reflux, which was maintained for two more hours. Rapid filtration of the warm solution afforded an orange–yellow solid. Yield, 0.122 g, 40.8%. Anal. Calc. for $C_{28}H_{24}CdHg_2N_2O_2S_2\cdot\frac{1}{2}EtOH$: C 33.69; H 2.81; N 2.42; S 6.42. Found: C 34.13; H 2.54; N 2.84; S 6.64%. IR (cm^{-1}) 2907 ν(C–H), 1605 ν(C=N), 1530 and 1320 ν(C–O).

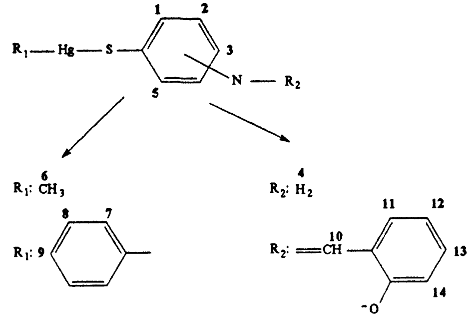
2.3. X-ray crystallography

Crystals were examined and data collected on a Stoe–Siemens four-circle diffractometer (**5** and **8**) and on a Bruker AXS SMART CCD diffractometer (**2**, **3** and **7**), in all cases with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) and at low temperature. Crystal data are given in Table 1. Semi-empirical absorption corrections were based on measurements of equivalent reflections. The structures were solved by standard heavy-atom and direct methods, and were refined on all unique F^2 values [10]. Disorder was resolved for one ligand and for both OH groups in compound **8**, with the aid of geometrical and displacement parameter restraints in refinement. Hydrogen atoms were located in difference syntheses for compounds **2**, **3** and **7** and were refined with appropriate constraints for C–H groups, but they were not located for compounds **5** and **8**. The largest residual electron density peaks are close to heavy atoms. The crystal of compound **5** was probably racemically twinned, with a refined enantiopole parameter of 0.46(2) [11].

Table 1
Crystallographic data for [Hg(4-$SC_6H_4NH_2$)$_2$] (**2**), [CH_3Hg(3-$SC_6H_4NH_2$)] (**3**), [PhHg(3-$SC_6H_4NH_2$)] (**5**), [CH_3Hg(3-$SC_6H_4N{=}CHC_6H_4OH$)] (**7**), [CH_3Hg(4-$SC_6H_4N{=}CHC_6H_4OH$)] (**8**)

	2	**3**	**5**	**7**	**8**
Formula	$C_{12}H_{12}HgN_2S_2$	C_7H_9HgNS	$C_{12}H_{11}HgNS$	$C_{14}H_{13}HgNOS$	$C_{14}H_{13}HgNOS$
M	449.0	339.8	401.9	443.9	443.9
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$Pna2_1$	$C2/c$	$P\bar{1}$
Unit cell dimensions					
a (Å)	4.3066(3)	8.1782(10)	7.172(2)	20.265(2)	7.068(3)
b (Å)	27.483(2)	10.2859(13)	14.215(3)	6.8258(8)	13.687(5)
c (Å)	10.7052(8)	10.6757(14)	23.597(5)	40.774(5)	14.781(6)
α (°)		102.286(2)			101.74(3)
β (°)	92.785(2)	91.214(2)		93.966(3)	96.42(3)
γ (°)		91.164(3)			102.83(3)
V (Å^3)	1265.5(2)	877.0(2)	2405.6(9)	5626.5(11)	1346.5(9)
Z	4	4	8	16	4
D_{calc} (g cm^{-3})	2.356	2.574	2.219	2.096	2.190
μ (mm^{-1})	12.47	17.71	12.94	11.08	11.57
T (K)	160	160	160	160	160
Crystal size (mm)	0.36 × 0.16 × 0.04	0.44 × 0.44 × 0.18	0.55 × 0.10 × 0.08	0.54 × 0.10 × 0.08	0.52 × 0.12 × 0.03
θ_{max} (°)	25.5	25.5	25.0	25.7	25.0
Transmission factor range	0.230–0.777	0.154–0.953	0.663–0.932	0.093–0.382	0.058–0.536
Reflections measured	5446	7560	3203	11630	6732
Unique reflections	2099	2872	2947	4673	4740
R_{int}	0.0951	0.1144	0.0401	0.0878	0.0503
Number of parameters	167	197	142	330	410
R (F, $F^2 > 2\sigma$)	0.0584	0.0582	0.0359	0.0591	0.1054
R_w (F^2, all data)	0.1526	0.1776	0.0888	0.1251	0.2617
Goodness of fit	1.199	1.167	1.045	1.216	1.145
Maximum, minimum electron density (e Å^{-3})	2.29, −3.53	3.40, −2.55	2.40, −1.61	1.48, −1.43	4.12, −4.50

Table 2
^{1}H-NMR data[a] (ppm) in DMSO at room temperature for complexes [Hg(3-SC$_6$H$_4$NH$_2$)$_2$] (**1**), [Hg(4-SC$_6$H$_4$NH$_2$)$_2$] (**2**), [CH$_3$Hg(3-SC$_6$H$_4$NH$_2$)] (**3**), [CH$_3$Hg(4-SC$_6$H$_4$NH$_2$)] (**4**), [PhHg(3-SC$_6$H$_4$NH$_2$)] (**5**), [PhHg(4-SC$_6$H$_4$NH$_2$)] (**6**), [CH$_3$Hg(3-SC$_6$H$_4$N=CHC$_6$H$_4$OH)] (**7**), [CH$_3$Hg(4-SC$_6$H$_4$N=CHC$_6$H$_4$OH)] (**8**), [PhHg(3-SC$_6$H$_4$N=CHC$_6$H$_4$OH)] (**9**), [PhHg(4-SC$_6$H$_4$N=CHC$_6$H$_4$OH)] (**10**), [Zn{CH$_3$Hg(3-SC$_6$H$_4$N=CHC$_6$H$_4$O)}$_2$] (**11**), [Zn{CH$_3$Hg(4-SC$_6$H$_4$N=CHC$_6$H$_4$O)}$_2$] (**12**)



Compound	H$_1$	H$_2$	H$_3$	H$_4$	H$_5$	H$_6$	H$_7$	H$_8$	H$_9$	H$_{10}$	H$_{11}$	H$_{12}$	H$_{13}$	H$_{14}$
3-HSC$_6$H$_4$NH$_2$	6.46 (d)	6.92 (t)	6.39 (d)	5.00 (s)	6.55 (s)									
1	6.50 (d)	6.80 (t)	6.29 (d)	5.01 (s)	6.60 (s)									
3	6.48 (d)	6.78 (t)	6.25 (d)	4.94 (s)	6.58 (s)	0.66 (s)								
5	6.56 (d)	6.82 (t)	6.28 (d)	4.99 (s)	6.66 (s)		7.47 (d)	7.31 (t)	7.20 (t)					
7	7.32 (d)	7.24 (t)	7.09 (d)		7.42 (s)	0.71 (s)				8.93 (s)	7.67 (d)	6.97 (t)	7.42 (t)	6.96 (d)
9	7.39 (d)	7.26 (t)	7.10 (d)		7.50 (s)		7.48 (d)	7.33 (t)	7.21 (t)	8.93 (s)	7.64 (d)	6.97 (t)	7.41 (t)	6.96 (d)
11	7.23 (d)	7.12 (t)	6.95 (d)		7.28 (s)	0.65 (s)				8.73 (s)	7.49 (d)	6.64 (t)	7.35 (t)	6.72 (d)
4-HSC$_6$H$_4$NH$_2$	7.09 (d)	6.53 (d)		5.47 (s)										
2	7.02 (d)	6.40 (d)		4.99 (s)										
4	6.99 (d)	6.40 (d)		4.87 (s)		0.62 (s)								
6	7.08 (d)	6.43 (d)		4.89 (s)			7.38 (d)	7.30 (t)	7.18 (t)					
8	7.42 (d)	7.25 (d)				0.69 (s)				8.92 (s)	7.60 (d)	6.95 (t)	7.41 (t)	6.93 (d)
10	7.51 (d)	7.28 (d)					7.49 (d)	7.33 (t)	7.20 (t)	8.92 (s)	7.60 (d)	6.96 (t)	7.38 (t)	6.94 (d)
12	7.31 (d)	7.11 (d)				0.65 (s)				8.75 (s)	7.49 (d)	6.65 (t)	7.34 (t)	6.71 (d)

[a] s singlet, d doublet, t triplet.

Table 3
Coupling constants (Hz) for complexes [Hg(3-$SC_6H_4NH_2$)$_2$] (**1**), [Hg(4-$SC_6H_4NH_2$)$_2$] (**2**), [CH_3Hg(3-$SC_6H_4NH_2$)] (**3**), [CH_3Hg(4-$SC_6H_4NH_2$)] (**4**), [PhHg(3-$SC_6H_4NH_2$)] (**5**), [PhHg(4-$SC_6H_4NH_2$)] (**6**), [CH_3Hg(3-$SC_6H_4N{=}CHC_6H_4OH$)] (**7**), [CH_3Hg(4-$SC_6H_4N{=}CHC_6H_4OH$)] (**8**), [PhHg(3-$SC_6H_4N{=}CHC_6H_4OH$)] (**9**), [PhHg(4-$SC_6H_4N{=}CHC_6H_4OH$)] (**10**), [Zn{CH_3Hg(3-$SC_6H_4N{=}CHC_6H_4O$)}$_2$] (**11**), [Zn{CH_3Hg(4-$SC_6H_4N{=}CHC_6H_4O$)}$_2$] (**12**)

Compound	$^3J(H_1–H_2)$	$^3J(H_2–H_3)$	$^4J(H_1–H_3)$	$^2J(Hg–H_6)$	$^3J(H_7–H_8)$	$^3J(H_8–H_9)$	$^3J(H_{11}–H_{12})$	$^3J(H_{12}–H_{13})$	$^3J(H_{13}–H_{14})$
3-$HSC_6H_4NH_2$	8.39	8.08							
1	7.93	7.32	1.22						
3	7.11	8.07	1.62	167.97					
5	7.33	7.93			7.32	7.32			
7	8.05	8.04	2.19	173.28			8.05	8.05	8.05
9	8.05	8.05					8.04	8.05	8.05
11	7.94	7.94		170.31			7.93	7.93	8.23
4-$HSC_6H_4NH_2$	8.74								
2	8.41								
4	8.04			165.24					
6	8.10				7.35	7.35			
8	8.05			173.28			8.05	8.05	8.05
10	8.04				7.31	7.31	8.04	8.05	8.05
12	8.55			175.19			7.94	7.97	8.54

3. Results and discussion

3.1. Complexes of formula [Hg(n-$SC_6H_4NH_2$)$_2$], n = 3 (1) or 4 (2) and [RHg(n-$SC_6H_4NH_2$)], R = Me, n = 3 (3) or 4 (4); R = Ph, n = 3 (5) or 4 (6)

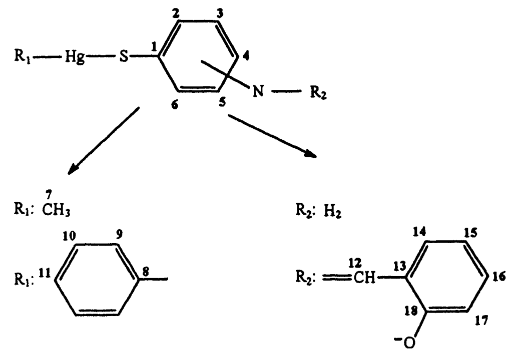
The reaction of [Hg(CH_3COO)$_2$], MeHgOH and PhHgCH_3COO with the aromatic aminothiols 3-$SC_6H_4NH_2$ and 4-$SC_6H_4NH_2$ produces the title complexes **1**–**6** with relatively good yields. They are slightly soluble in common organic low coordinating solvents such as CH_3CN, $CHCl_3$ and EtOH. However, considering complexes **3**–**6**, solubility increases if the compound contains the (3-$SC_6H_4NH_2$)$^-$ aminothiolate ligand and/or the MeHg$^+$ species. Complexes **1**–**6** show a significant tendency to decompose, mainly in solution but also in the solid phase, yielding elemental mercury and the corresponding disulfide. This tendency increases with temperature, and solid complexes containing MeHg$^+$ are unstable above 8–10°C. Accordingly, all complexes have to be kept at low temperature. Analogous redox decomposition has already been reported for solid [Hg(SPh)$_2$] at 240°C [12].

Complexes **1**–**6** have been fully characterized by ^{1}H and ^{13}C-NMR spectroscopies (Tables 2–4 respectively). The assignment of the signals has been deduced by standard calculations and by comparison with the free ligands and related literature data. In addition, ^{199}Hg-NMR data (Table 5) have allowed determination of the coordination geometry about mercury(II) in solution. In order to diminish considerably the registration time of the ^{199}Hg-NMR spectrum without decreasing the signal-to-noise ratio, we have used the INEPT [13] and RINEPT [14] pulse sequences for complexes **3** and **4** of formula [MeHg($SC_6H_4NH_2$)]. Unfortunately, the absence of protons with a measurable coupling constant with the mercury nucleus in **1**, **2**, **5** and **6** hinders the use of the previous sequences. The ^{199}Hg chemical shift values found for **1**, **2** and for **3**, **4** (Table 5) are, respectively, within the ranges given in the literature for [Hg(SR)$_2$] and [MeHg(SR)] compounds [2,15,16] containing Hg(II) with digonal coordination. Reported data for [PhHgX] complexes reduce to X = inorganic anions [17] and they are not therefore a good reference for establishing the coordination geometry of Hg(II) in [PhHg(SR)] complexes **5**, **6**. On the other hand, considering that the ^{199}Hg resonances indicate that the secondary Hg···S interactions present in the solid phase of **2** and **3** are absent in solution, it seems likely that the same behaviour could be extended to **5**. Thus, the fact that its X-ray structure consists of linear C–Hg–S units enables us to propose that the experimental chemical shift values of − 948 and − 963 ppm are indicative of digonal coordination about Hg(II) in **5** and **6**, respectively.

The crystal structures of [Hg(4-$SC_6H_4NH_2$)$_2$] (**2**), [MeHg(3-$SC_6H_4NH_2$)$_2$] (**3**) and [PhHg(3-$SC_6H_4NH_2$)$_2$ (**5**) have been solved by X-ray diffraction. Selected bond lengths and angles are given in Tables 6–8. The Hg–S distance in the basic units of the three complexes (Figs. 1–3) lies within the range 2.35–2.39 Å and consequently it is in good concordance with the sum of covalent radii of diagonally coordinated mercury with sulfur atoms [18], and with that found in closely related species [17,19].

The asymmetric unit of **2**, one quarter of the unit cell, contains one molecule of [Hg(4-$SC_6H_4NH_2$)$_2$] as shown in Fig. 1a. The Hg atom presents a linear two-coordination, with the S–Hg–S angle only slightly bent (175.7°). The two Hg–S bonds are effectively

Table 4
^{13}C-NMR data in DMSO at room temperature for complexes [Hg(3-$SC_6H_4NH_2$)$_2$] (**1**), [Hg(4-$SC_6H_4NH_2$)$_2$] (**2**), [CH_3Hg(3-$SC_6H_4NH_2$)] (**3**), [CH_3Hg(4-$SC_6H_4NH_2$)] (**4**), [PhHg(3-$SC_6H_4NH_2$)] (**5**), [PhHg(4-$SC_6H_4NH_2$)] (**6**), [CH_3Hg(3-$SC_6H_4N{=}CHC_6H_4OH$)] (**7**), [CH_3Hg(4-$SC_6H_4N{=}CHC_6H_4OH$)] (**8**), [PhHg(3-$SC_6H_4N{=}CHC_6H_4OH$)] (**9**), [PhHg(4-$SC_6H_4N{=}CHC_6H_4OH$)] (**10**), [Zn{CH_3Hg(3-$SC_6H_4N{=}CHC_6H_4O$)}$_2$] (**11**), [Zn{CH_3Hg(4-$SC_6H_4N{=}CHC_6H_4O$)}$_2$] (**12**)



Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{115}	C_{16}	C_{17}	C_{18}
3-$HSC_6H_4NH_2$	136.96	121.23	134.67	116.43	154.29	118.76												
1	136.58	119.84	129.06	117.13	148.84	111.02												
3	137.90	119.81	128.96	117.46	148.81	110.46	11.76											
5	137.78	119.78	129.11	110.64	148.93	117.37		161.51	137.22	128.46 [a]	127.99 [a]							
7	140.11	129.34	130.51	117.52	148.40	119.46	11.47					163.43	124.57	132.49	119.05	133.34	116.70	160.49
9	140.14	129.52	130.64	117.72	148.40	119.49		161.02	137.25	128.43	127.96	163.69	124.67	132.72	119.30	133.49	116.75	160.49
11	140.48	129.28	130.42	117.35	148.43	122.63	11.47					170.72	124.68	135.85	118.60	137.48	114.56	170.10
4-$HSC_6H_4NH_2$	120.79	134.20	114.11	149.85														
2	124.05	138.70	119.58	151.87														
4	120.44	133.63	114.74	146.30			11.86											
6	120.16	133.64	114.79	146.48				161.90	137.26	128.49 [a]	127.96 [a]							
8	138.14	133.11	119.56	144.50			11.53					162.11	121.79	132.64	119.35	133.26	116.79	160.47
10	133.52	132.64[a]	119.23	144.55				161.96	136.99	128.17	127.70	160.14	121.50	132.32 [a]	119.00	132.99	116.44	160.05
12	138.13	135.72	122.57	144.69			11.33					169.00	121.19	132.90	118.62	137.39	114.64	170.52

[a] The proximity of each pair of values does not allow definite assignment.

Table 5
^{199}Hg-NMR spectroscopic data of complexes **1**–**6**

Complex	δ ^{199}Hg (ppm) [a]
[Hg(3-$SC_6H_4NH_2$)$_2$] (**1**)	−1079 (s)
[Hg(4-$SC_6H_4NH_2$)$_2$] (**2**)	−1135 (s)
[MeHg(3-$SC_6H_4NH_2$)$_2$] (**3**)	−613 (q)
[MeHg(4-$SC_6H_4NH_2$)$_2$] (**4**)	−645 (q)
[PhHg(3-$SC_6H_4NH_2$)$_2$] (**5**)	−948 (s)
[PhHg(4-$SC_6H_4NH_2$)$_2$] (**6**)	−963 (s)

[a] s singlet, q quartet.

Table 6
Selected bond distances (Å) and angles (°) for [Hg(4-$SC_6H_4NH_2$)$_2$] (**2**); in this and other tables, primed atoms are related to unprimed atoms by various symmetry operations

Hg(1)–S(1)	2.361(3)	Hg(1)–S(2)	2.352(3)
S(1)–C(11)	1.784(13)	S(2)–C(21)	1.787(12)
Hg(1)–S(2′)	3.252(3)	Hg(1)–S(1′)	3.185(3)
Hg(1)–S(1″)	3.146(3)		
S(1)–Hg(1)–S(2)	175.75(11)	C(21)–S(2)–Hg(1)	101.7(4)
C(11)–S(1)–Hg(1)	103.3(4)	S(2′)–Hg(1)–S(1′)	177.12(8)
S(1)–Hg(1)–S(1″)	84.06(10)	S(1)–Hg(1)–S(2′)	79.12(9)

Table 7
Selected bond distances (Å) and angles (°) for [CH_3Hg(3-$SC_6H_4NH_2$)] (**3**)

Hg(1)–C(11)	2.074(14)	Hg(2)–C(21)	2.092(16)
Hg(1)–S(1)	2.373(4)	Hg(2)–S(2)	2.379(4)
S(1)–C(12)	1.747(15)	S(2)–C(22)	1.756(14)
Hg(1)–N(2)	2.920(12)	Hg(2)–N(1′)	2.905(13)
Hg(1)–S(2′)	3.417(4)	Hg(1)–S(1′)	3.507(4)
C(11)–Hg(1)–S(1)	175.5(5)	C(21)–Hg(2)–S(2)	174.8(5)
C(12)–S(1)–Hg(1)	105.6(5)	C(22)–S(2)–Hg(2)	105.0(5)
S(1)–Hg(1)–S(1′)	91.28(11)	S(2)–Hg(2)–S(2′)	94.71(10)

Table 8
Selected bond distances (Å) and angles (°) for [PhHg(3-$SC_6H_4NH_2$)] (**5**)

Hg(1)–C(7)	2.058(14)	Hg(2)–C(19)	2.074(15)
Hg(1)–S(1)	2.363(4)	Hg(2)–S(2)	2.364(4)
S(1)–C(1)	1.81(2)	S(2)–C(13)	1.76(2)
Hg(1)–S(1′)	3.229(5)	Hg(2)–S(1′)	3.250(7)
Hg(1)–S(2′)	3.185(7)	Hg(2)–S(2′)	3.357(5)
C(7)–Hg(1)–S(1)	174.9(6)	C(19)–Hg(2)–S(2)	178.2(7)
C(1)–S(1)–Hg(1)	102.3(6)	C(13)–S(2)–Hg(2)	105.4(6)
S(1′)–Hg(1)–S(1)	89.88(11)	S(1′)–Hg(2)–S(2)	83.72(18)
S(2′)–Hg(1)–S(1)	85.22(17)	S(2′)–Hg(2)–S(2)	92.38(13)
C(7)–Hg(1)–S(1′)	95.0(5)	C(19)–Hg(2)–S(1′)	97.8(8)
S(2′)–Hg(1)–S(1′)	73.21(14)	S(2′)–Hg(2)–S(1′)	70.71(14)
S(2′)–Hg(1)–C(7)	97.4(8)	S(2′)–Hg(2)–C(19)	89.1(5)

equal (2.352(3), 2.361(3) Å). The mercury atom of each basic unit interacts with three neighbouring units by means of Hg···S secondary bonds having an average distance of 3.19 Å, significantly shorter than the sum of the corresponding van der Waals radii (3.5 Å [2]). Thus, the coordination number of Hg increases to 5 (2 + 3 in terms of primary and secondary interactions) with adoption of square-based pyramidal geometry (Fig. 1b), giving a chain polymer along the unit cell *a* axis. The core of the chain contains parallel S–Hg–S primary units and is formed by fused Hg_3S_4 incomplete cubanes when the secondary interactions are also considered; it is surrounded by a sheath of radiating aromatic substituents, all approximately parallel.

The asymmetric unit of **3** is half a unit cell and consists of two crystallographically independent [MeHg(3-$SC_6H_4NH_2$)$_2$] molecules (Fig. 2a). Hg coordination is essentially linear, with an average C–Hg–S angle of 175.5°, and the Hg–S and Hg–C distances are in good agreement with literature data for related compounds [17]. Each of these two molecules forms a centrosymmetric dimer with a symmetry-related molecule through secondary Hg···S bonds, and the *anti*-disposed aromatic substituents are approximately perpendicular to the central Hg_2S_2 core (dihedral angles of 88.7 and 85.3°), minimizing possible steric interactions within the dimeric units. Further secondary bonding, between amino groups and mercury, links the dimers into sheet networks (Fig. 2b). The average Hg···N distance is 2.9 Å, less than the sum of the van der Waals radii (3.3 Å [2]). As a result, the coordination number of Hg should be considered as 2 + 2, with a geometry best regarded as pseudo-octahedral with two *cis*-positions vacant.

The crystal structure of **5** also has two crystallographically independent molecules in the asymmetric unit, which is here one quarter of the unit cell. The two molecules of [PhHg(3-$SC_6H_4NH_2$)$_2$] differ significantly only in the orientations of the aromatic substituents (Fig. 3a). The average C–Hg–S angle for the essentially linear coordination geometry is 176.6°. Each mercury atom has two secondary Hg···S interactions with average distance 3.26 Å, to give 2 + 2 coordination, and the result is a linking of the individual molecules into a polymeric zig-zag ladder (Fig. 3b), surrounded by a sheath of radiating aromatic substituents. The ladder may be considered as composed of pseudo-cubanes, each having one face opened up by lengthening of two opposite Hg···S edges, and sharing opposite faces.

3.2. Complexes of formula [RHg(n-$SC_6H_4N{=}CHC_6H_4OH$)] R = Me, n = 3 (*7*) or 4 (*8*); R = Ph, n = 3 (*9*) or 4 (*10*)

The synthetic procedures followed for obtaining complexes **7**–**10** have afforded moderate-to-good yields. Their solubility in common organic solvents is dependent on the nature of R and the value of *n*. Thus, complexes with R = Me are clearly more soluble than those with R = Ph. Within each group, complexes with $n = 3$ are more soluble than those with $n = 4$. The main feature of the infrared spectrum of **7–10** is the absorption band at about 1280 cm^{-1}, which corresponds to the stretching frequency of the C–O group in *N*-arylsalicylaldimines [18] and is thus indicative of the presence of the condensed salicylaldehyde. Complexes **7–10** have been characterized by ^{1}H and ^{13}C-NMR as shown in Tables 2–4, respectively. In the ^{1}H-NMR spectrum of **7–10** the resonance at ca. 9 ppm and the absence of that at ca. 5 ppm, due to the N–CH and NH$_2$ protons,

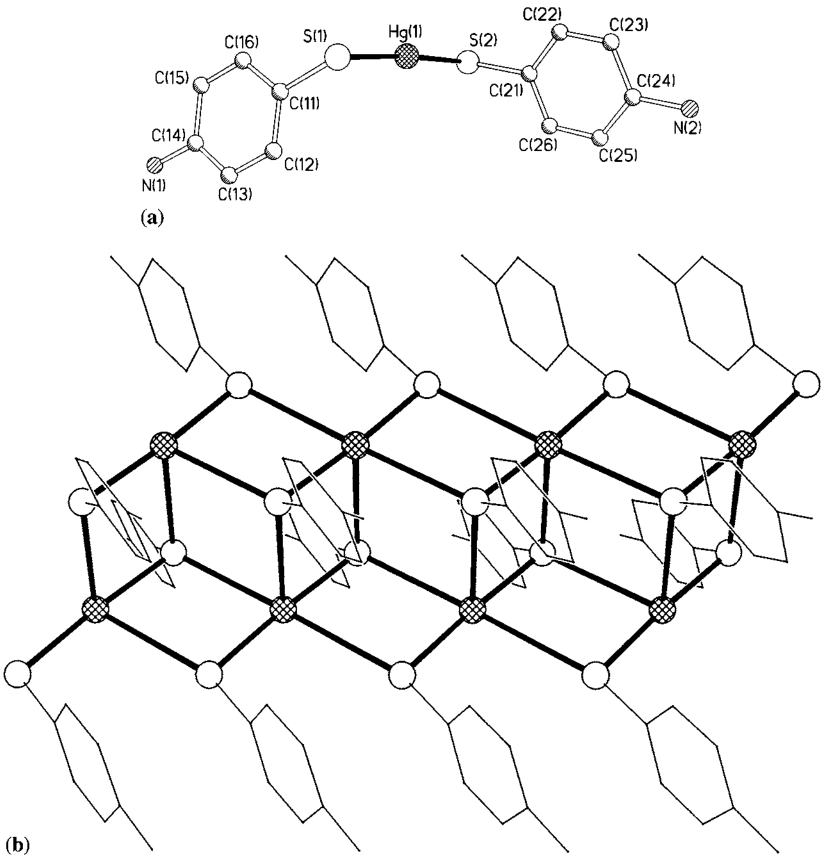


Fig. 1. The structure of [Hg(4-SC$_6$H$_4$NH$_2$)$_2$] (**2**): (a) the asymmetric unit without H atoms, showing atom numbering; (b) a section of the polymeric chain of linked incomplete Hg$_3$S$_4$ cubanes.

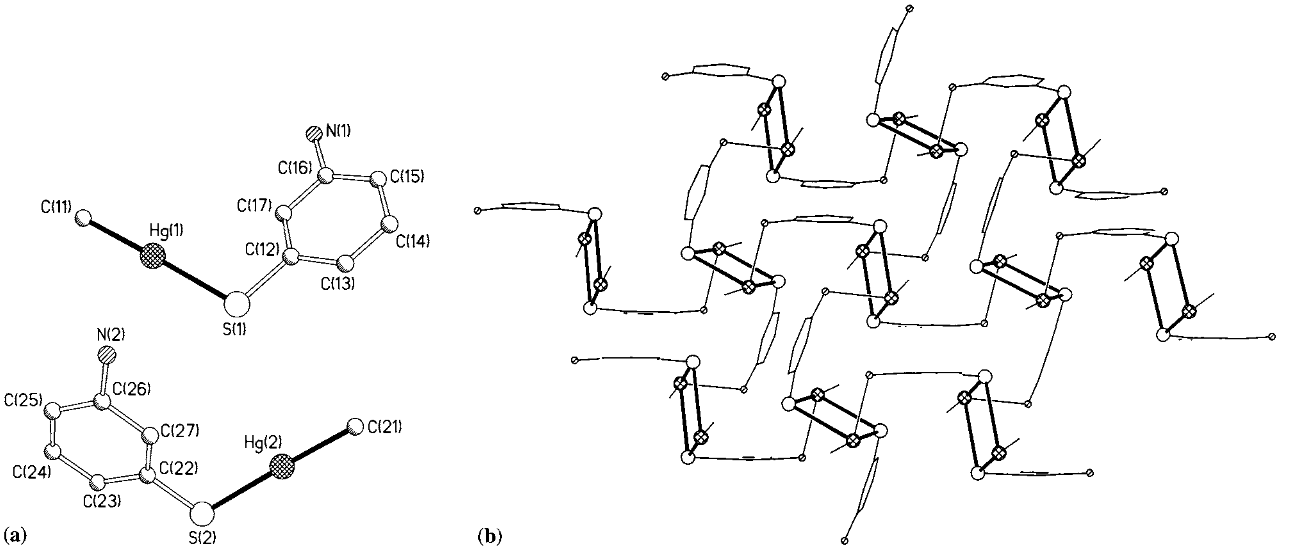


Fig. 2. The structure of [MeHg(3-SC$_6$H$_4$NH$_2$)$_2$] (**3**): (a) the asymmetric unit without H atoms, showing the atom numbering; (b) part of the sheet network resulting from Hg···S and Hg···N secondary interactions.

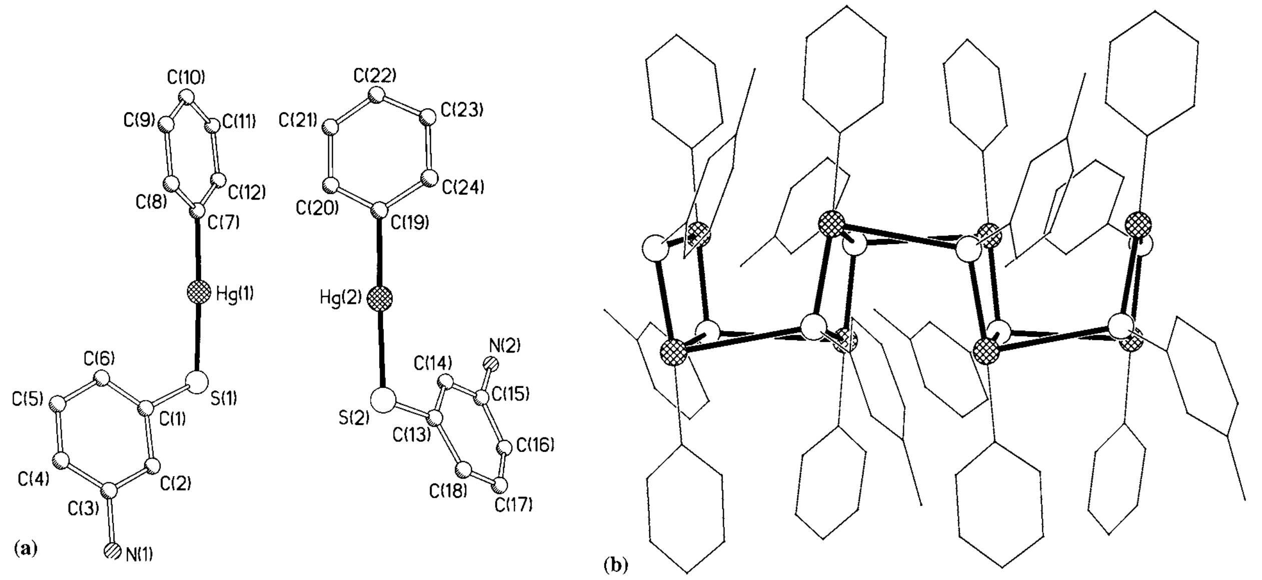


Fig. 3. The structure of [PhHg(3-$SC_6H_4NH_2$)$_2$] (**5**): (a) the asymmetric unit without H atoms, showing the atom numbering; (b) a section of the zig-zag ladder formed through Hg···S interactions.

respectively, are indicative of the formation of the Schiff base. However, owing to the complexity of the aromatic region in these spectra (**7**, **8** and **9**, **10** contain two and three aromatic rings, respectively), 2D ^{1}H-NMR spectra were also recorded. These, together with the ^{1}H-NMR data of the uncondensed parent amine complexes **3**–**6** and of the free salicylaldehyde allowed definite assignment of all ^{1}H resonances in complexes **7**–**10**. Their ^{13}C-NMR spectrum also shows a considerable number of peaks due to the aromatic carbon nuclei within the range 115–140 ppm. The tentative assignment of these resonances (Table 4) has been based on standard calculations considering the *n*-$HSC_6H_4N{=}C{-}HC_6H_4OH$ molecule and on comparison among the four complexes. In this case, the parent complexes **3**–**6** cannot be taken as reference, given that their ^{13}C resonances shift 1–6 ppm upon formation of the Schiff base.

The molecular structures of complexes **7** and **8** are closely related, and so they are described together (Tables 9 and 10). The asymmetric unit in each case consists of two independent molecules of [MeHg(*n*-$SC_6H_4N{=}CHC_6H_4OH$)] with $n = 3$ for **7** (Fig. 4a) and 4 for **8** (Fig. 5a). There are no significant differences in the geometric parameters for the primary coordination of the metal centres in these two structures. In each case the mercury coordination is essentially linear (average C–Hg–S angles 178.5 and 176.4°), and overall geometric features are similar to those of compound **3**. However, in both structures the further Hg···S secondary interactions raise the coordination number to 2 + 2 and produce the same kind of ladder polymer as for **5**, shown in different views in Fig. 4b and Fig. 5b. The ladder for **8** is somewhat more distorted than that for **7**. The asymmetric unit is one eighth of the unit cell in **7** and one half of the unit cell in **8**, but this difference affects the details of the packing of the individual ladders in the two crystal structures and not the overall form of these ladders themselves. The thiolate substituents have bond lengths and angles similar to those of related Schiff bases. Common to both **7** and **8** is the *E* disposition of the benzene rings within each substituent, minimizing steric repulsions, and the presence of intramolecular O–H···N hydrogen bonds between hydroxyl and imine groups; the average N···O distance for the two independent molecules of **7** is 2.62 Å, but

Table 9
Selected bond distances (Å) and angles (°) for [CH_3Hg(3-$SC_6H_4N{=}CHC_6H_4OH$)] (**7**)

Hg(1)–S(1)	2.383(3)	Hg(2)–S(2)	2.379(3)
Hg(1)–C(11)	2.071(12)	Hg(2)–C(21)	2.092(12)
S(1)–C(12)	1.767(13)	S(2)–C(22)	1.771(13)
Hg(1)–S(1′)	3.240(3)	Hg(2)–S(1′)	3.160(3)
Hg(1)–S(2′)	3.128(3)	Hg(2)–S(2′)	3.251(3)
C(11)–Hg(1)–S(1)	178.7(4)	C(21)–Hg(2)–S(2)	178.3(5)
C(12)–S(1)–Hg(1)	105.2(4)	C(22)–S(2)–Hg(2)	102.3(4)

Table 10
Selected bond distances (Å) and angles (°) for [CH_3Hg(4-$SC_6H_4N{=}CHC_6H_4OH$)] (**8**)

Hg(1)–S(1)	2.369(7)	Hg(2)–S(2)	2.384(8)
Hg(1)–C(1)	2.05(4)	Hg(2)–C(15)	2.11(3)
S(1)–C(2)	1.77(3)	S(2)–C(16)	1.74(3)
Hg(1)–S(1′)	3.491(7)	Hg(2)–S(1′)	3.294(8)
Hg(1)–S(2′)	3.353(7)	Hg(2)–S(2′)	3.316(7)
C(1)–Hg(1)–S(1)	176.5(11)	C(15)–Hg(2)–S(2)	176.2(10)
C(2)–S(1)–Hg(1)	100.7(9)	C(16)–S(2)–Hg(2)	96.7(11)

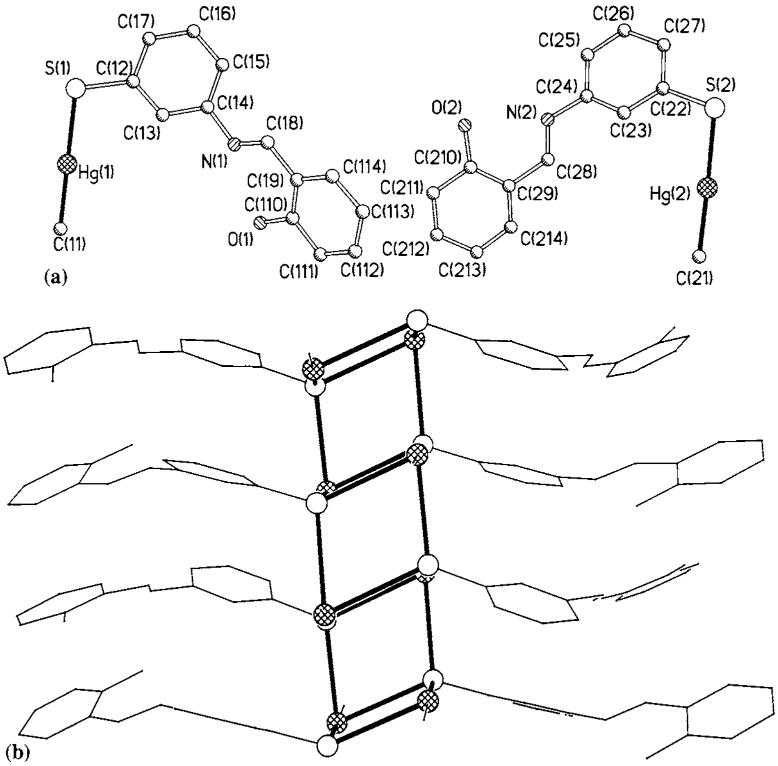


Fig. 4. The structure of [MeHg(3-$SC_6H_4N{=}CHC_6H_4OH$)] (**7**): (a) the asymmetric unit without H atoms, showing the atom numbering; (b) the ladder viewed from a direction approximately perpendicular to one equivalent to Fig. 3b.

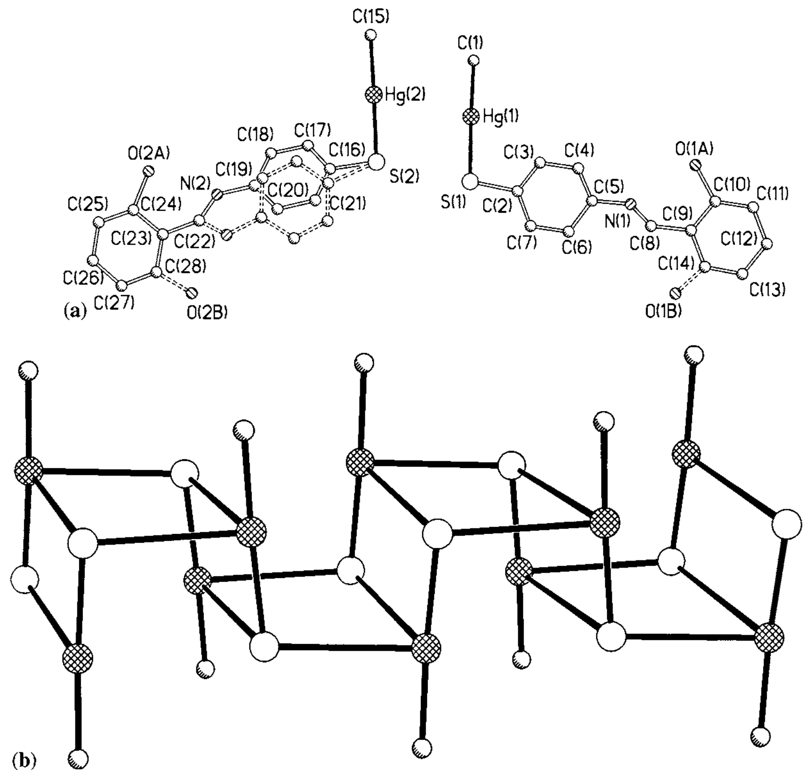


Fig. 5. The structure of [MeHg(4-$SC_6H_4N{=}CHC_6H_4OH$)] (**8**): (a) the asymmetric unit without H atoms, showing the atom numbering; (b) the core of the ladder structure common to this and compounds **5** and **7**.

the hydrogen bonding does not occur throughout the structure of **8** because of two-fold disorder in the orientations of the hydroxyphenyl groups (Fig. 5b).

3.3. Complexes of formula $[M^{II}\{MeHg(n\text{-}SC_6H_4N{=}CHC_6H_4O)\}_2]$, $M = Zn$, $n = 3$ (**11**) or 4 (**12**); $M = Cd$, $n = 3$ (**13**) or 4 (**14**)

The three basic synthetic procedures reported [19] in obtaining the title complexes can be summarized as follows: (i) reaction of metal ion and Schiff base in the presence of added base, (ii) reaction of primary amine with bis-(salicylaldehyde) metal complex, (iii) template reaction. All of these have been assayed for different divalent metals (Mn, Ni, Pd, Cu, Zn, Cd) with both aminothiolate derivatives of $MeHg^+$ and $PhHg^+$. However, the low solubility of the compounds or mixtures obtained has not allowed the synthesis of pure complexes except for **11**–**14**. For these complexes, the template reaction procedure has afforded the best yield for the shortest reaction time and for the minimum volume of solvent required to run the reaction in solution. Complexes **11** and **12** are somewhat soluble in most organic solvents. However, **13** and **14** are only soluble in hot DMSO, DMF and pyridine. As already described, complexes with $n = 3$ are more soluble than their analogues with $n = 4$. The main features of the infrared spectrum of **11**–**14** are in concordance with the coordination of Zn(II) and Cd(II) to the $[MeHg(n\text{-}SC_6H_4N{=}CHC_6H_4OH)]$ metalloligand by means of the imine N and the O atom of the deprotonated OH group. This is mainly shown by the frequency of the stretching vibration of C=N and C–O groups, which are shifted 5–30 cm^{-1} downwards and 30–50 cm^{-1} upwards, respectively, if compared with those of the parent complexes **7**–**10**. This coordination is confirmed by the ^1H and ^{13}C-NMR data of Zn(II) complexes **11** and **12**, Tables 2–4, respectively, as well as by preliminary information of the X-ray structure of **12**. The comparison of the ^1H-NMR data of **11** and **12** with those of **7** and **8**, respectively, shows a decrease in the degree of overlapping of the signals corresponding to the aromatic protons of the salicylaldehyde moiety. A similar comparison of the ^{13}C-NMR data indicates that the values of the chemical shifts corresponding to the carbon nuclei of C=N and C–O groups in **11** and **12** are shifted ca. 10 ppm downfield upon the complex formation. At this stage, the poor quality of the crystals obtained for **12** only allows us to infer that it has a trimetallic $ZnHg_2$ molecular structure with an essentially linear coordination of Hg to the methyl carbon and thiolate sulfur atoms, and with tetrahedral N_2O_2 coordination about the Zn atom. With regard to the Cd(II) complexes **13** and **14**, their low solubility in practically all solvents has hindered us from recording their ^1H and ^{13}C-NMR spectra, as well as from making attempts to obtain single crystals. Consequently, the use of specific strategies in order to increase the solubility of the complexes derived from $[RHg(n\text{-}SC_6H_4N{=}CHC_6H_4O)]$ metalloligands seems to be a prior requirement for pursuing their study.

4. Supplementary material

Five crystallographic files in CIF format have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 147377–147381. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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